

ポテンシャル曲面の化学(4)

あとで、クイズが出ます。
できるだけ、メモしておくことを、
オススメします。



7月22(金)9:00~

担当： 大野 公一

1. 化学とポテンシャル曲面

2. 化学結合ができる仕組み

3. 分子内ポテンシャルと分子振動

4. 分子間ポテンシャル

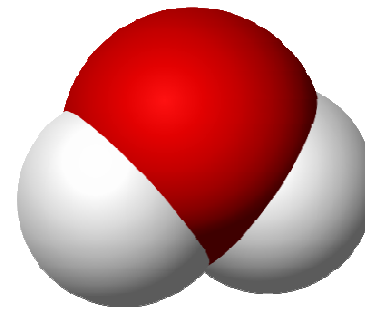
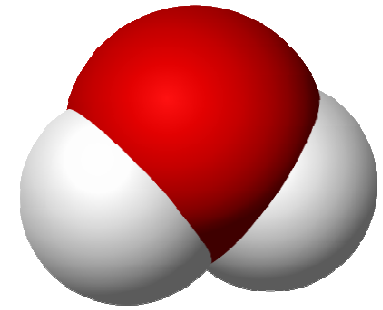
5. 原子と分子のポテンシャル

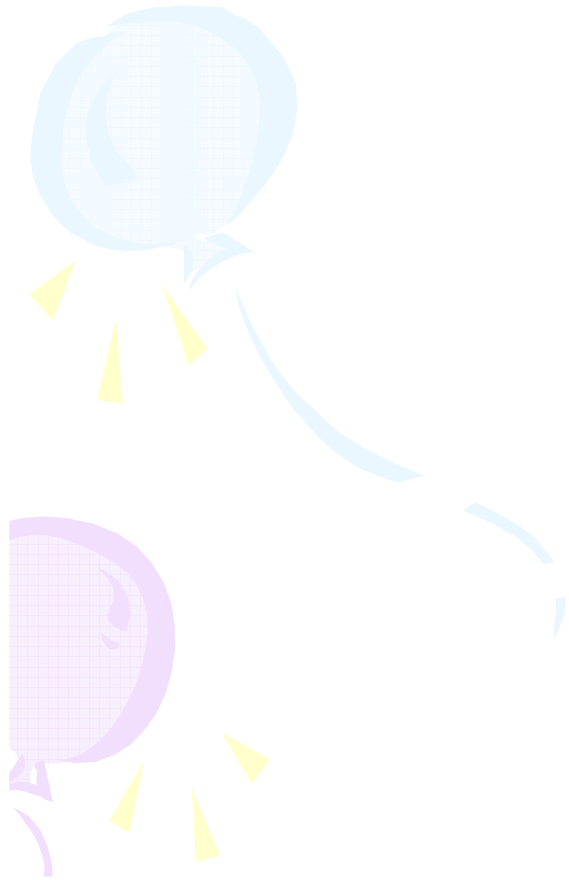
6. 化学反応とポテンシャル

分子間力

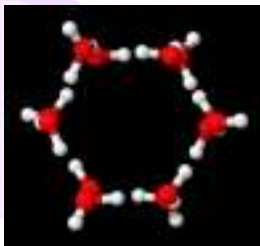
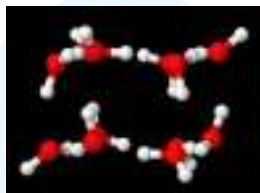
- イオン間相互作用
- 水素結合
- 双極子相互作用
- London分散力
(van der Waals力)
- 分子間の万有引力

H₂O分子どうしは、
どのような構造をとるか？

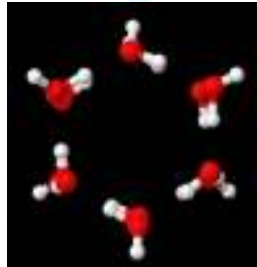
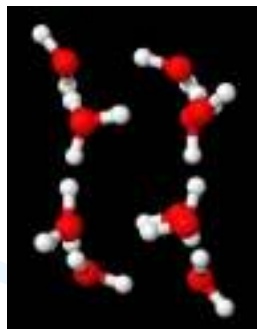
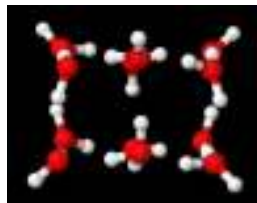




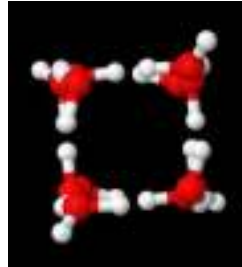
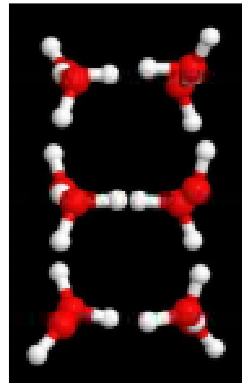
水の12量体クラスター $(\text{H}_2\text{O})_{12}$ の構造の 理論計算



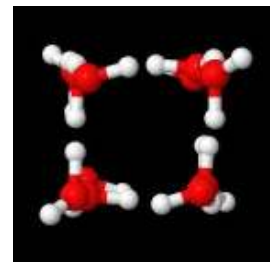
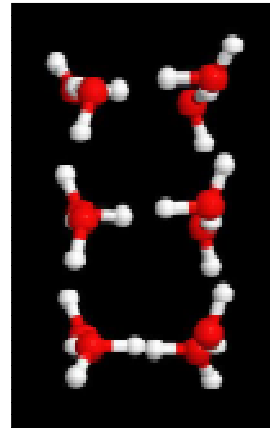
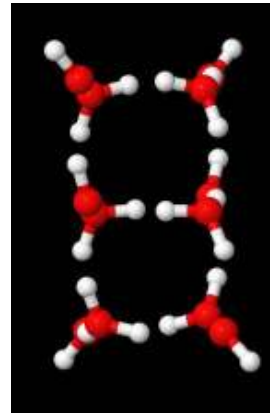
0.0 kJ/mol



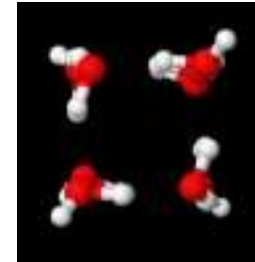
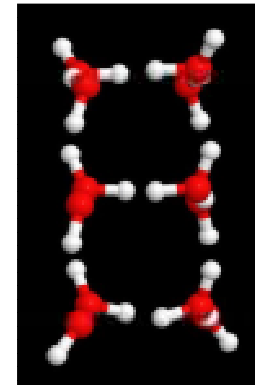
1.3 kJ/mol



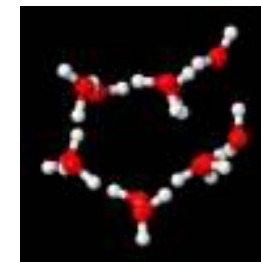
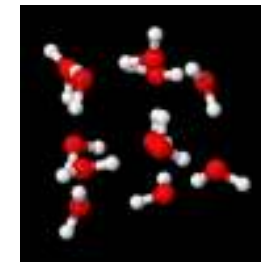
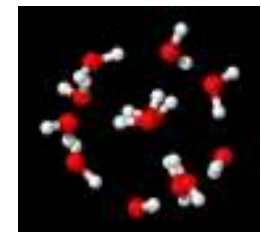
3.0 kJ/mol



4.3 kJ/mol

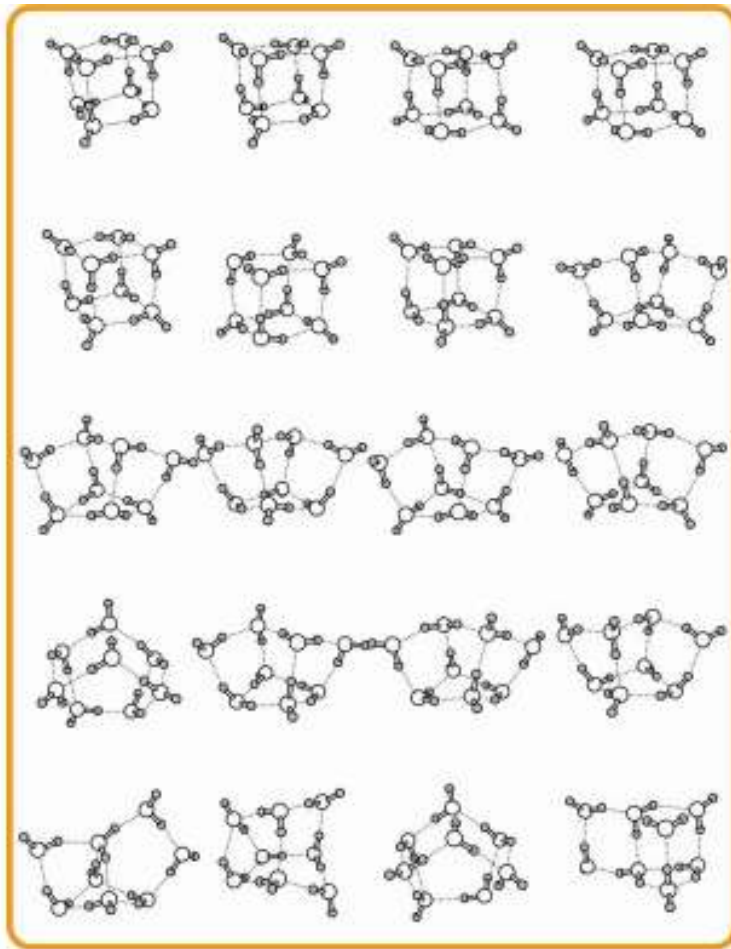


5.6 kJ/mol

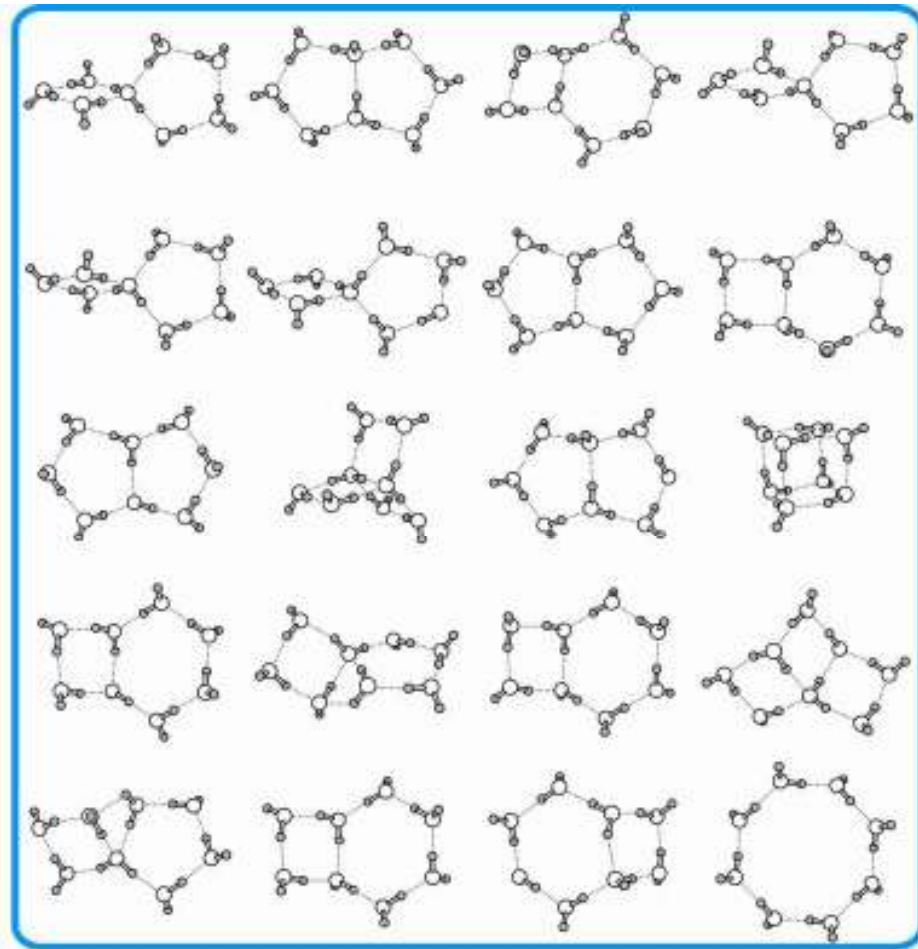


6.1 kJ/mol

水8量体の構造の温度依存性 (Gibbs自由エネルギーで比較)



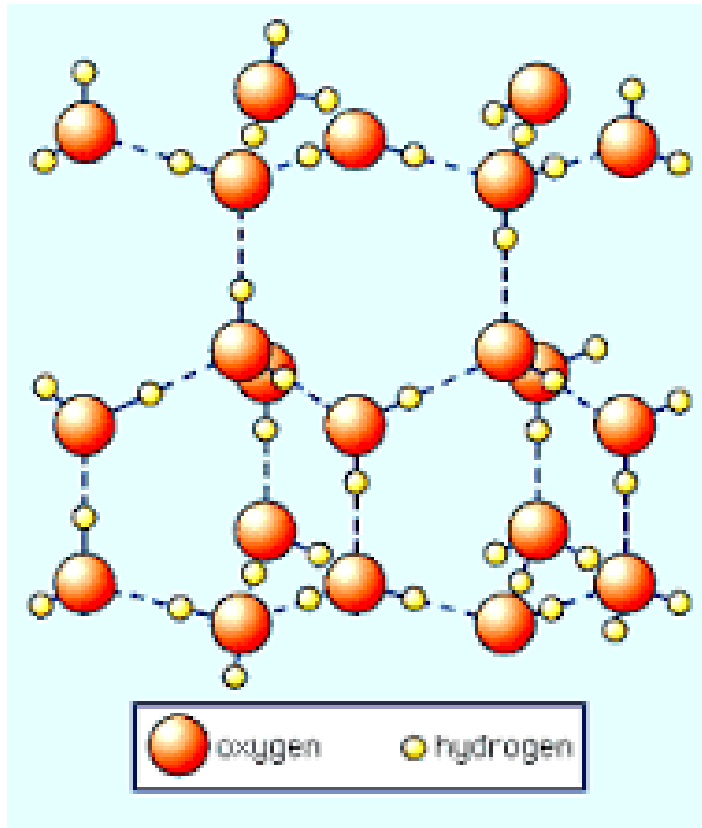
Lowest 20 minima at 0 K



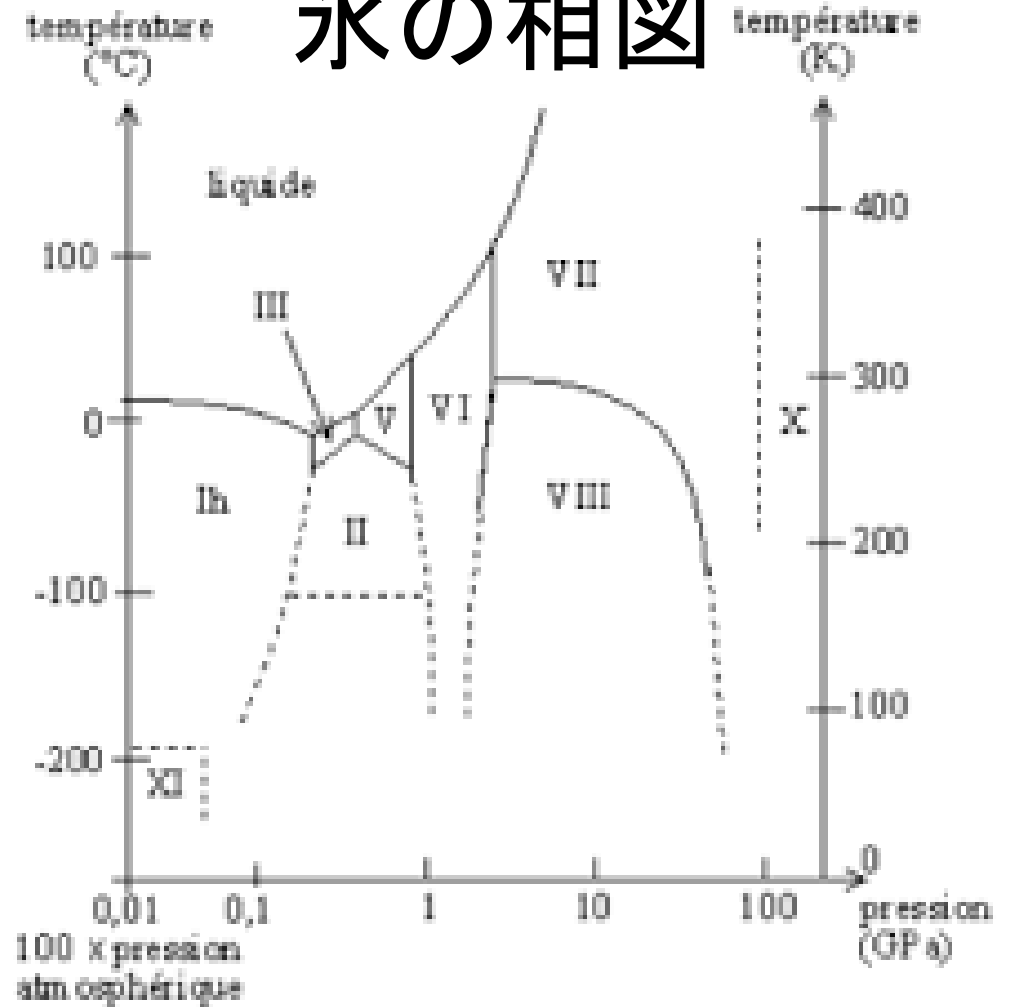
Lowest 20 minima at 400 K

氷の構造

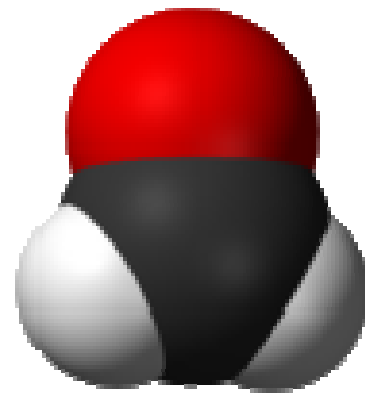
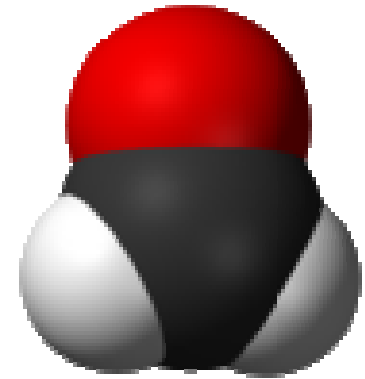
Ih型氷の構造



氷の相図

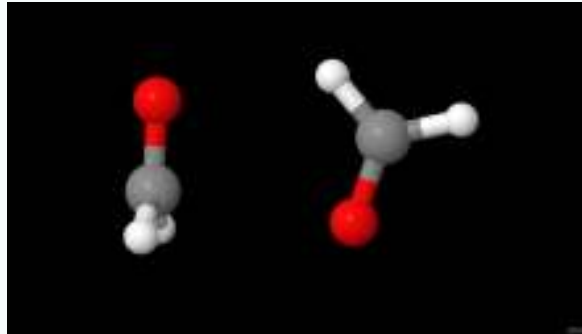


HCHO分子どうしは、
どのような構造をとるか？



Formaldehyde 2量体 (H₂CO)₂

C_s



C_{2h}



CCSD(T)/CBS : 0.0 kJ/mol

3.3 kJ/mol

C.A.Dolgonos, Chem.Phys.Lett. 585, 37 (2013).

M062X/6-311+G(2d,p)

0.0 kJ/mol

5.8 kJ/mol

MP2/ 6-31++G(2d,2p)

0.0 kJ/mol

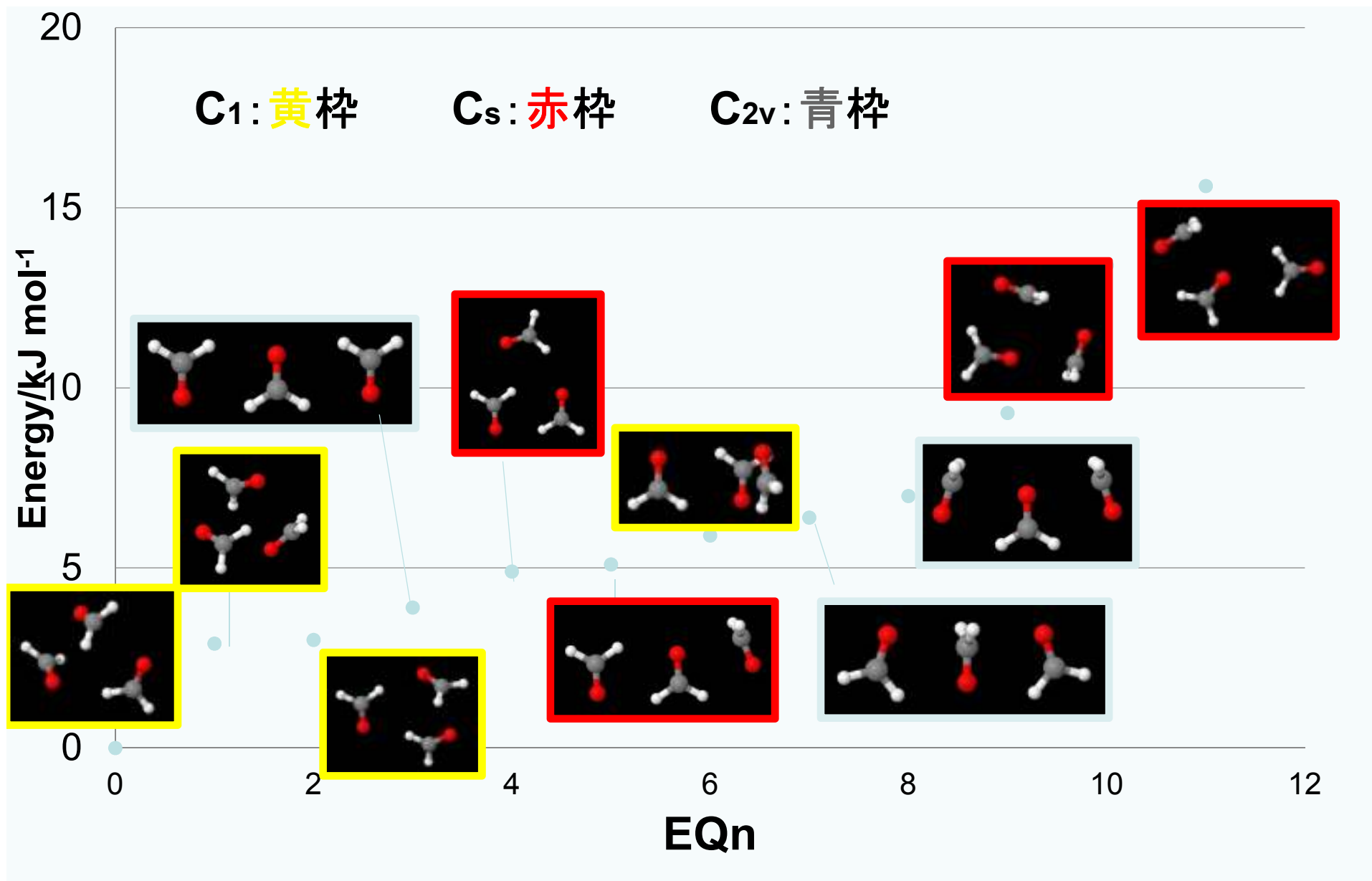
3.9 kJ/mol

MP2/ cc-pVTZ

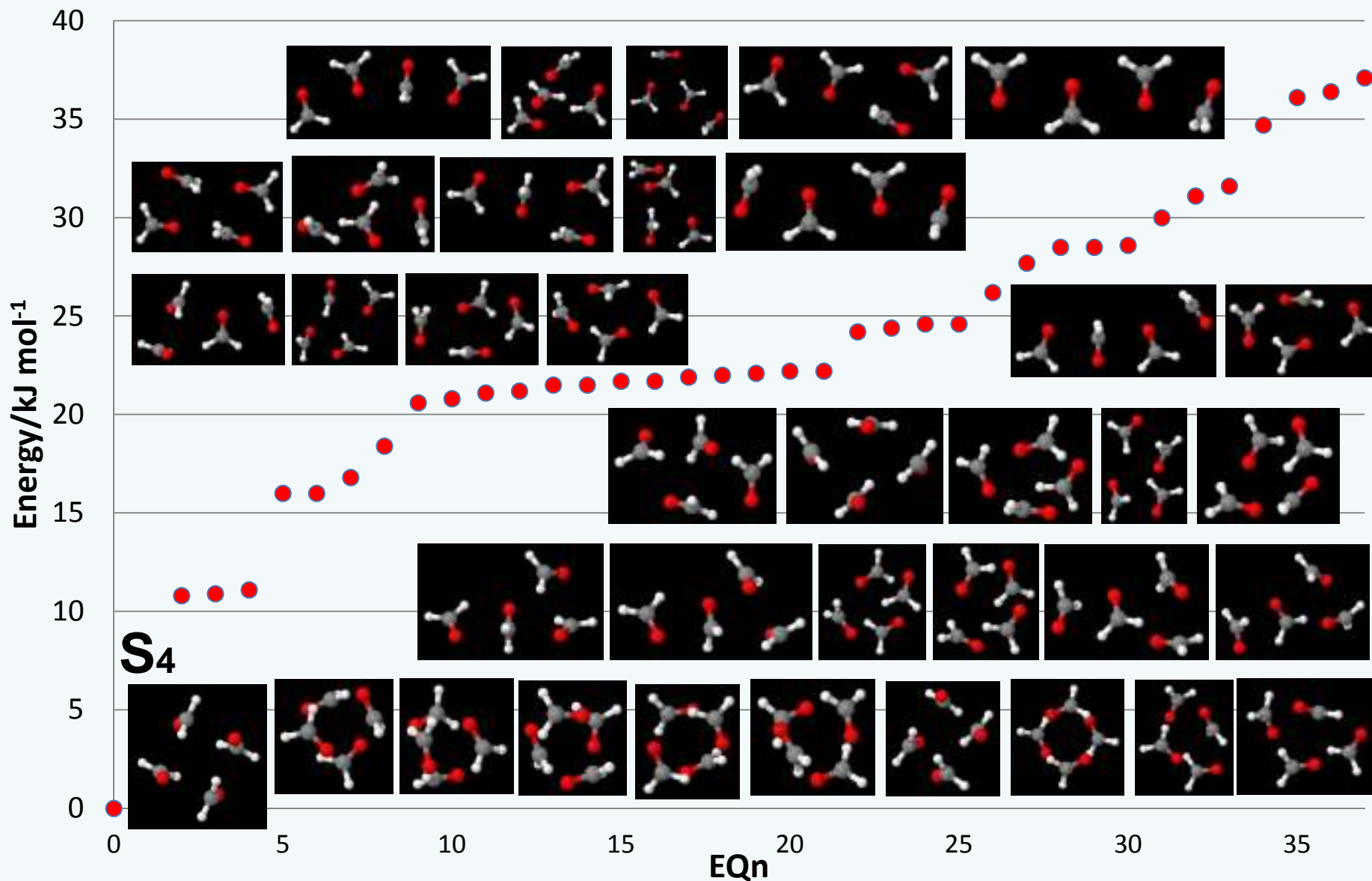
0.0 kJ/mol

1.7 kJ/mol

Formaldehyde 3量体 (H₂CO)₃

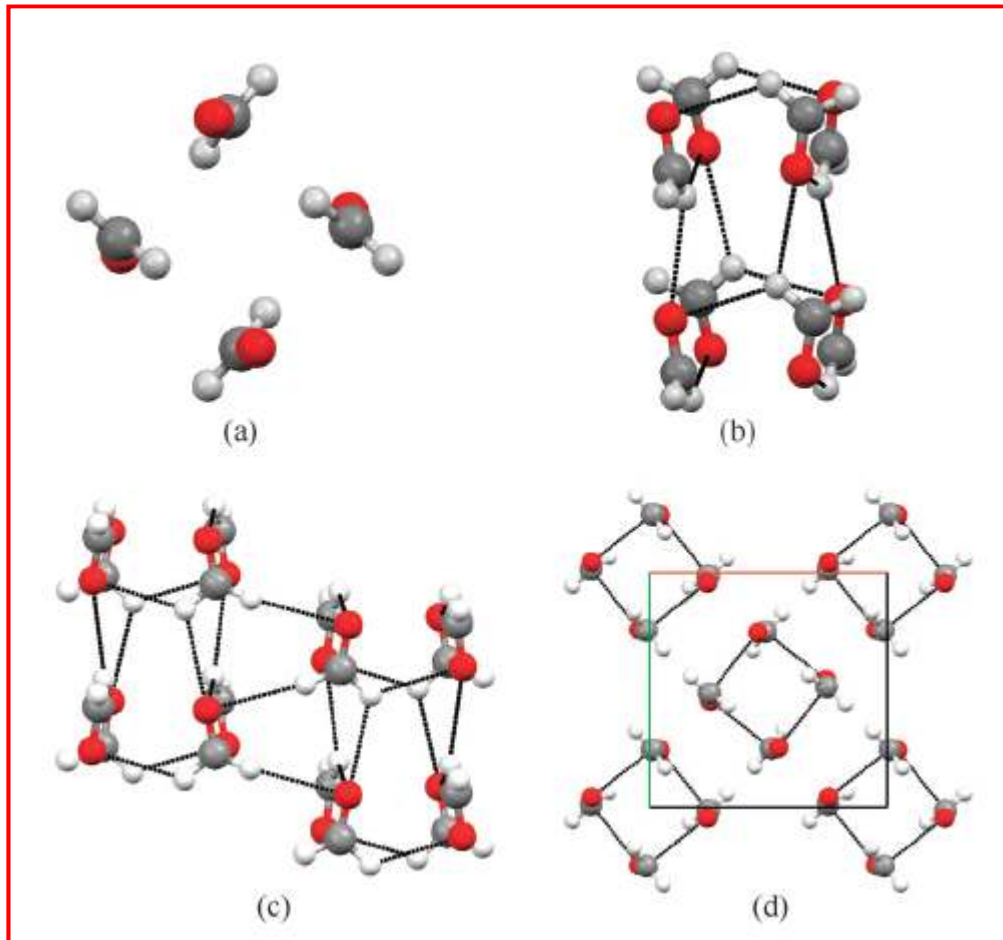


Formaldehyde 4量体(H₂CO)₄ 理論探索

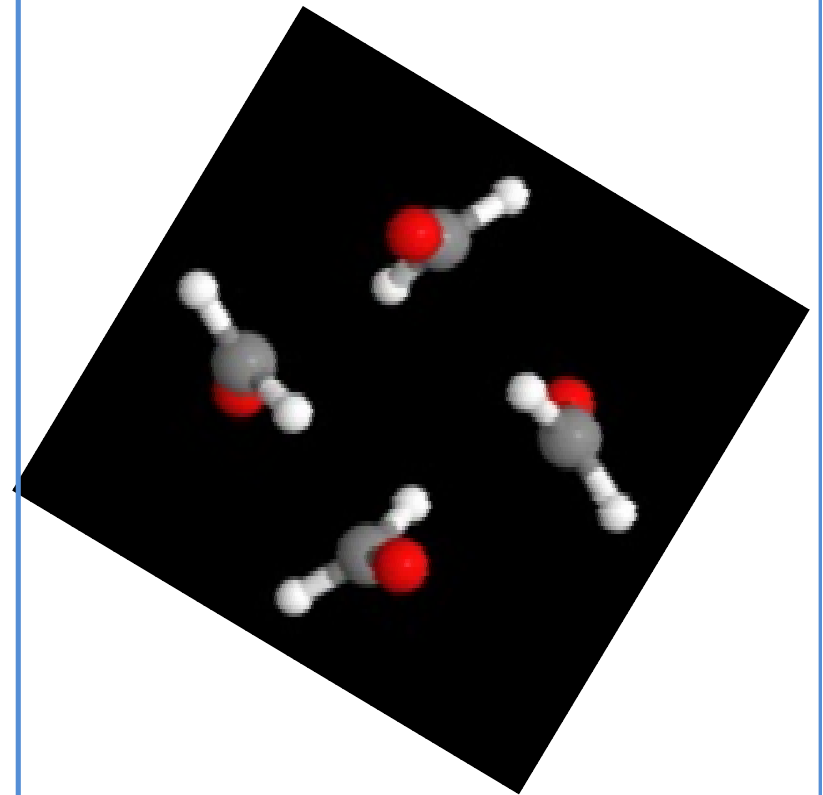


Formaldehydeの結晶構造と4量体

T.S.Thakur et al., PCCP, 13, 14076 (2011).



This work by GRRM :
LADD/Bond-Condition



結晶構造の予測は可能か？

分子どうしが触れ合って
反応することもある？

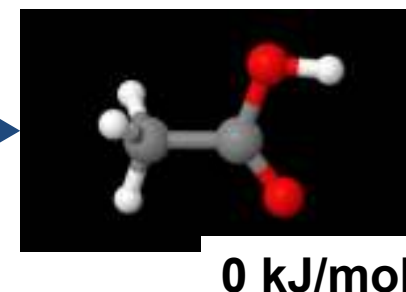
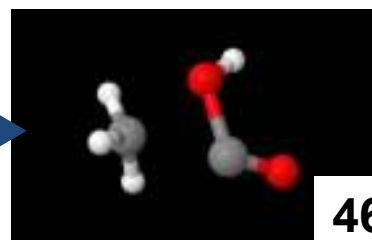
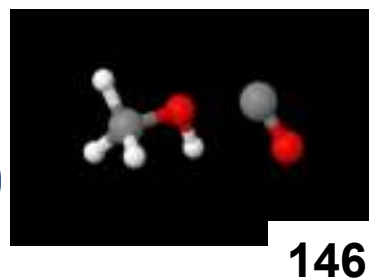
分子間反応



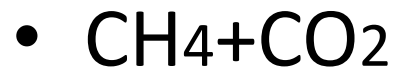
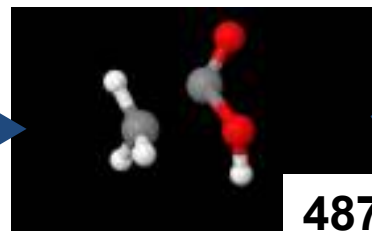
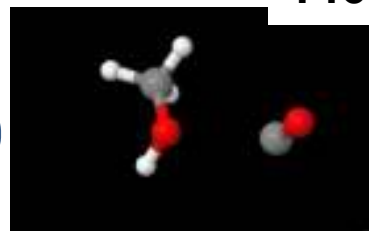
1-step synthesis of CH₃COOH



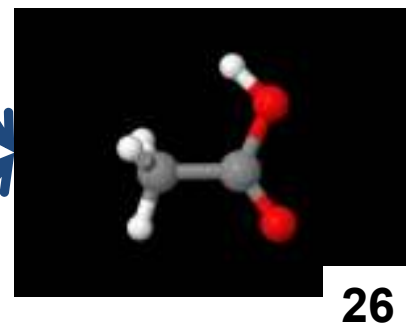
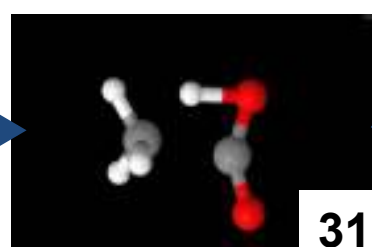
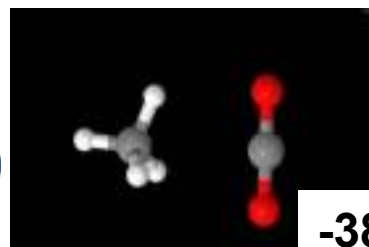
1



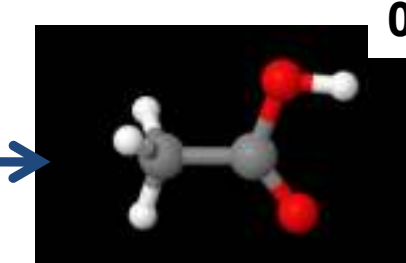
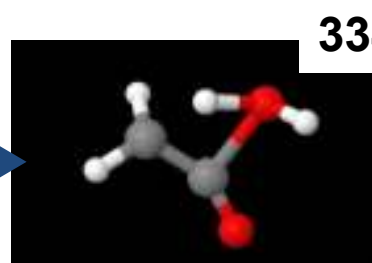
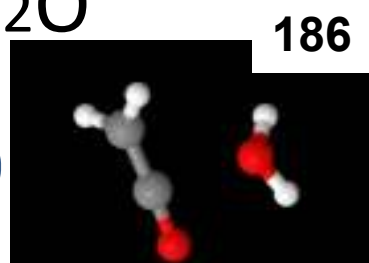
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3



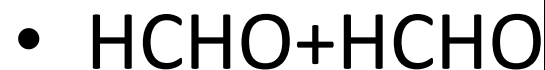
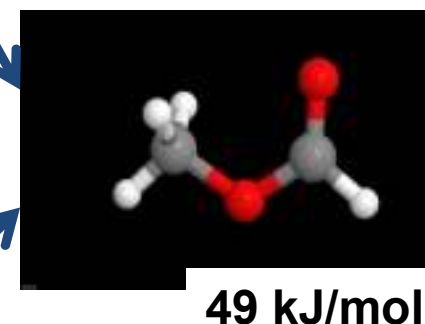
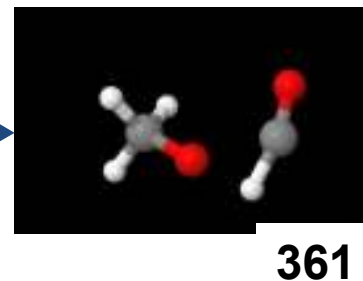
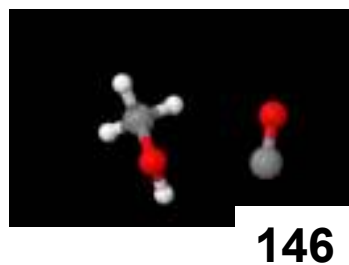
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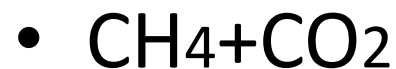
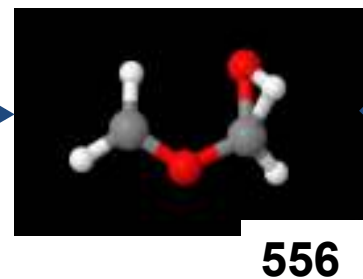
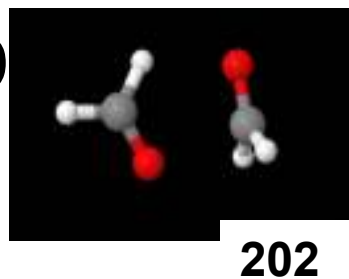
1-step synthesis of HCOOCH₃



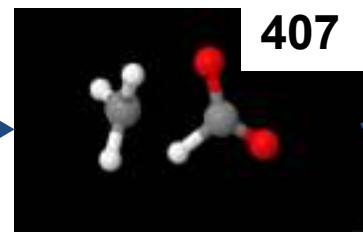
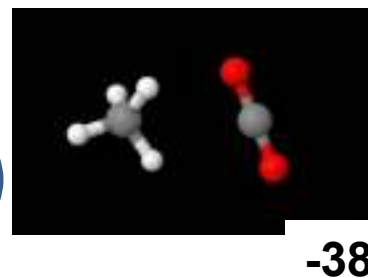
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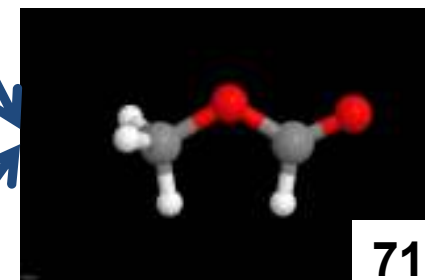
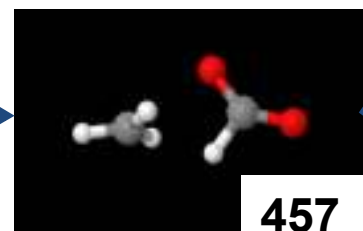
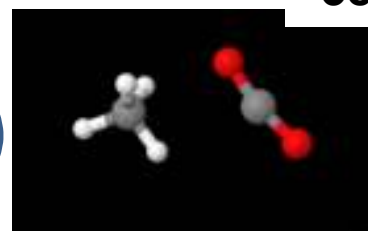
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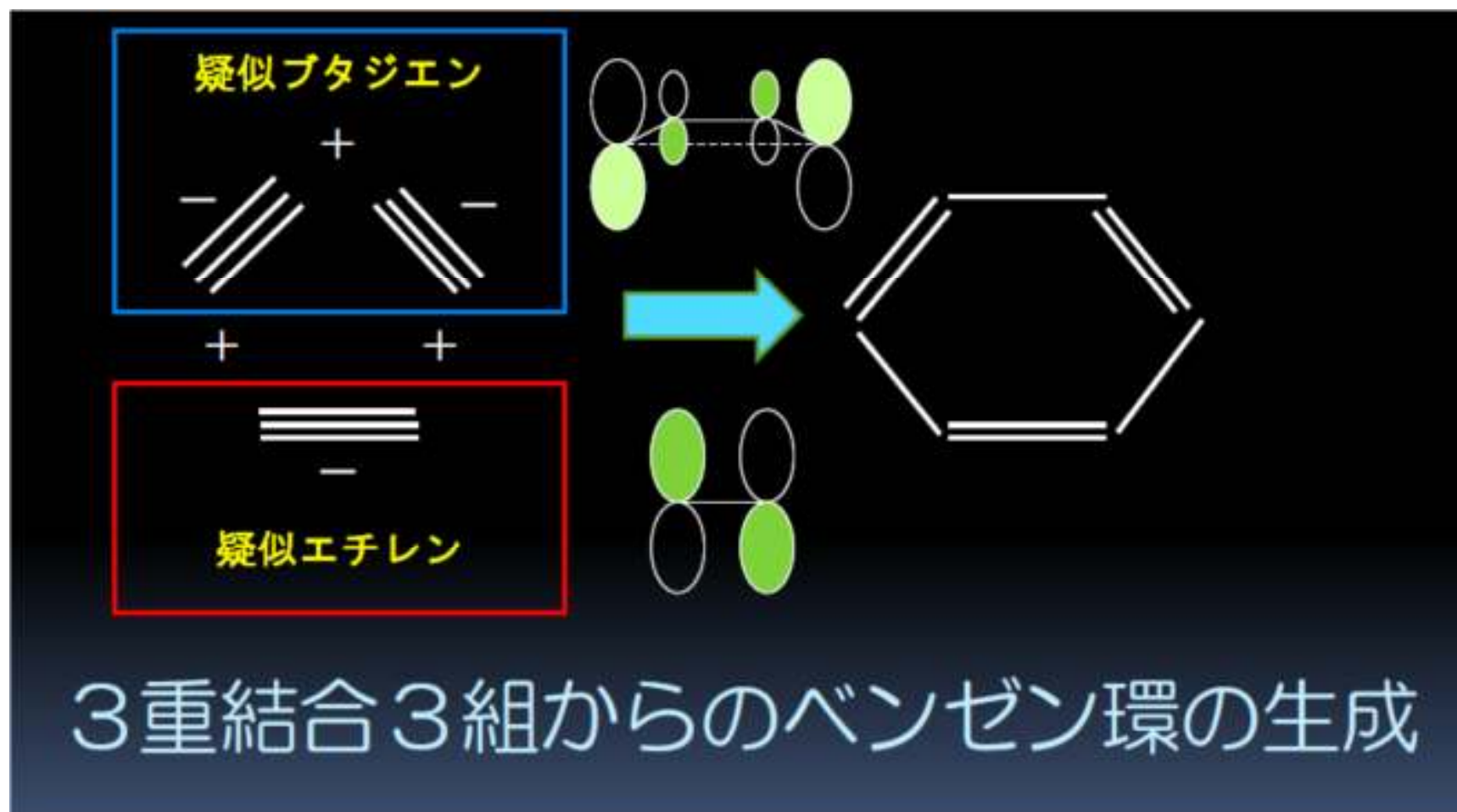
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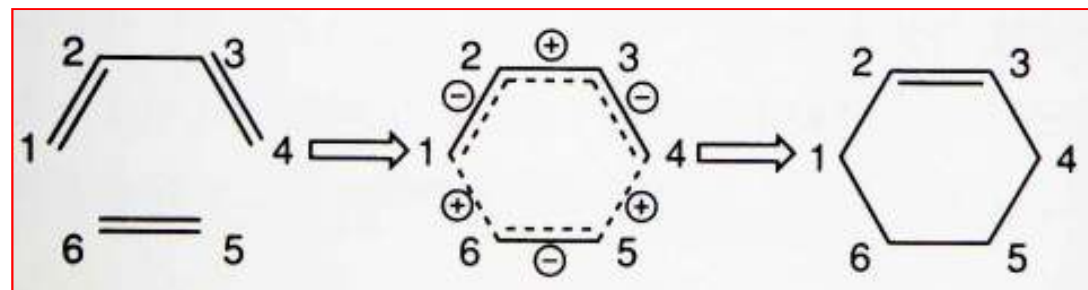
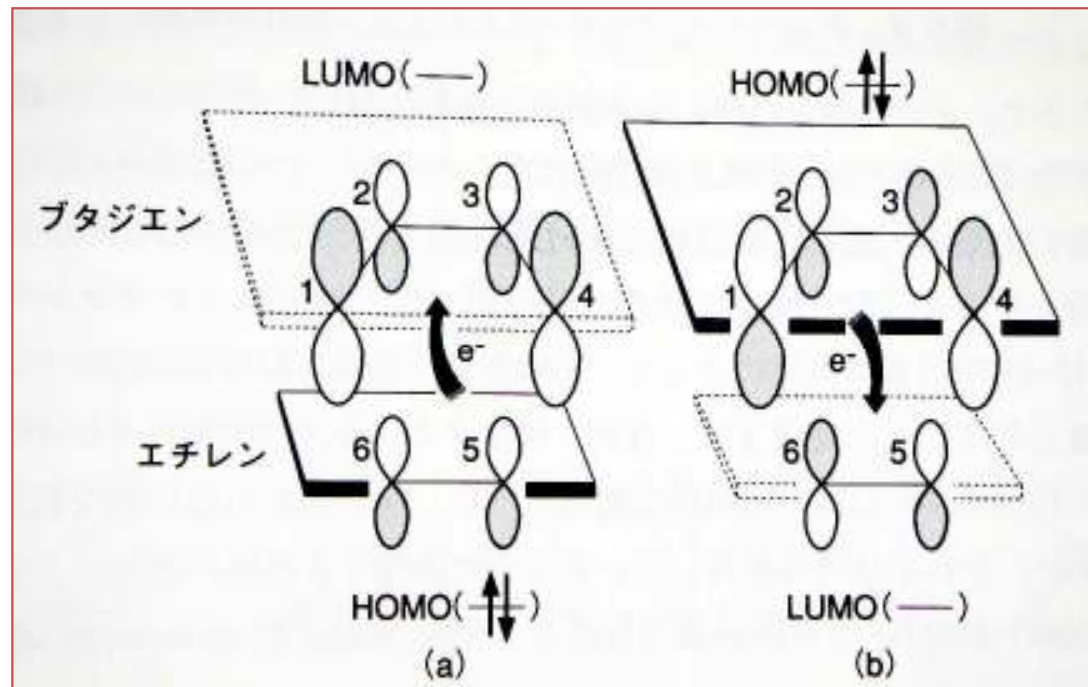
8



ベンゼンの合成



エチレンとブタジエンの HOMO-LUMO相互作用



アセチレン3分子から、
ベンゼンができる反応の仕組み？

1. 化学とポテンシャル曲面
2. 化学結合ができる仕組み
3. 分子内ポテンシャルと分子振動
4. 分子間ポテンシャル

Next → 5. 原子と分子のポテンシャル

6. 化学反応とポテンシャル