Topological study of chemical bonds under pressure: solid hydrogen

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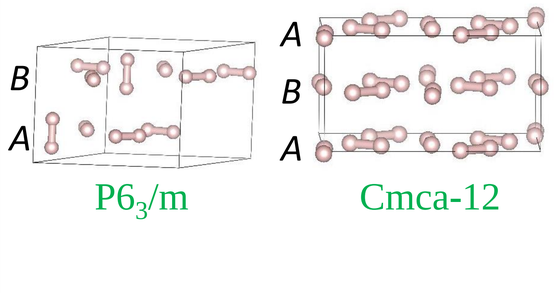
Introduction

H_2 is the simplest molecule and as any molecular solid, hydrogen is expected to polymerize under pressure. The comprehension of the mechanism by which this polymerization occurs is the main motivation for the work presented here. For that, we used a topological approach to reveal the process of polymerization using the NCI topological tool.[**1**] The current best plausible structural candidates for hydrogen under pressure were investigated theoretically in Refs [**2,3**].

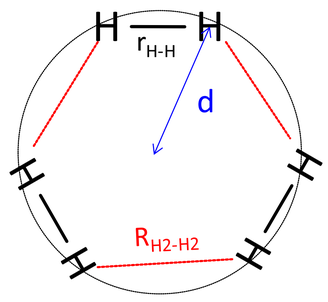
an *ABA* stacking | an *ABCD* stacking | monoatomic phase



$P6_3/m$ | Cmca-12 | Cmca | C2/c | $I4_1/amd$

The pressure range (GPa) of stability
$P6_3/m$: 0 < P < 105
C2/c: 105 < P < 270
Cmca-12: 270 < P < 385
Cmca: 385 < P < 490
$I4_1/amd$: 490 < P

To have a better understanding of this chemical bond transformation, we decided to computationally study the following molecular model:



- $3H_2$ molecules confined in a ring
- imposed D_{3h} symmetry
- the d distance adjusted to model the effect of pressure
- Wigner-seitz radius and d relationship: $2\pi d = 6(2r_s a_0)$
- molecular motif contained in C2/c and Cmca-12

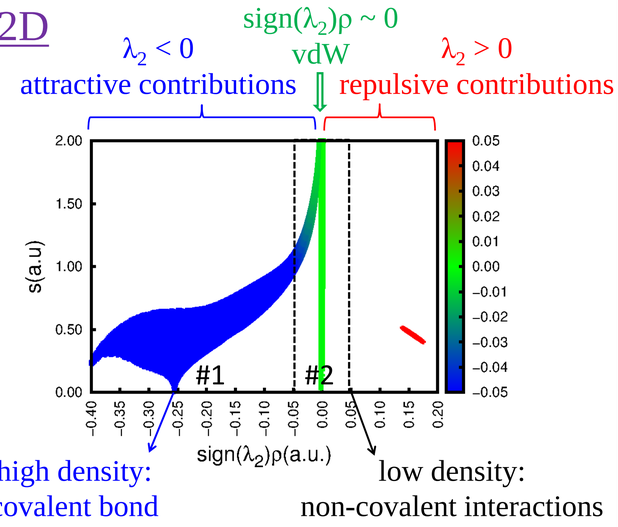
[**1**] *J. Am. Chem. Soc.* **132**, 6498 (2010). [**2**] *Nature Physics* **3**, 473 (2007). [**3**] *Phys. Rev. Lett.* **106**, 165302 (2011).

Theoretical background

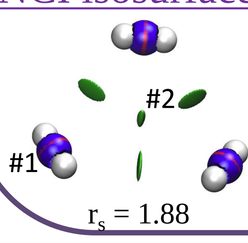
The NCI analysis is based on the electron density and its derivatives:

$$s(\rho) = \frac{|\nabla\rho|}{2(3\pi^2)^{\frac{1}{3}}\rho^{\frac{4}{3}}}$$

Plot 2D



NCI isosurfaces



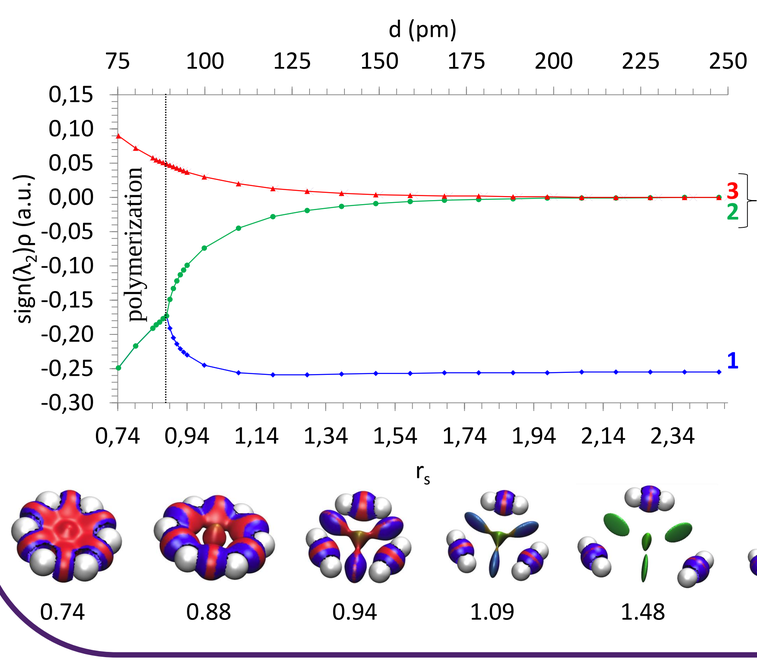
Integration

$$V_{NCI} = \int_{\Omega_{NCI}} d\vec{r}$$

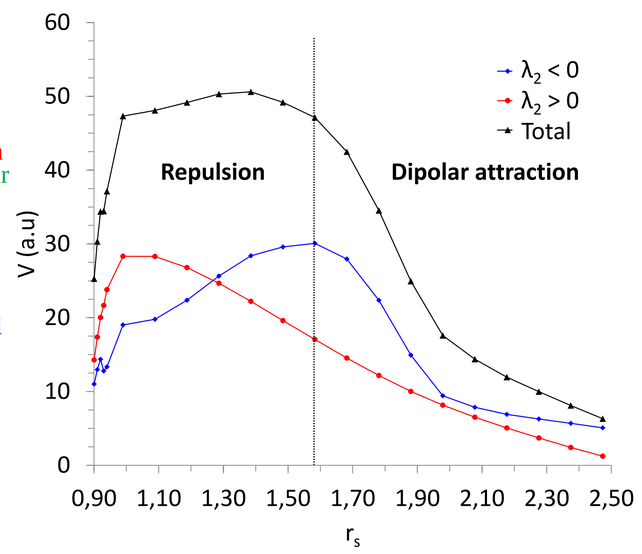
volume of the isosurface | NCI region

$3H_2$ molecular model

Evolution of sign(λ_2)ρ values of NCI peaks



Volume integrations within the NCI region



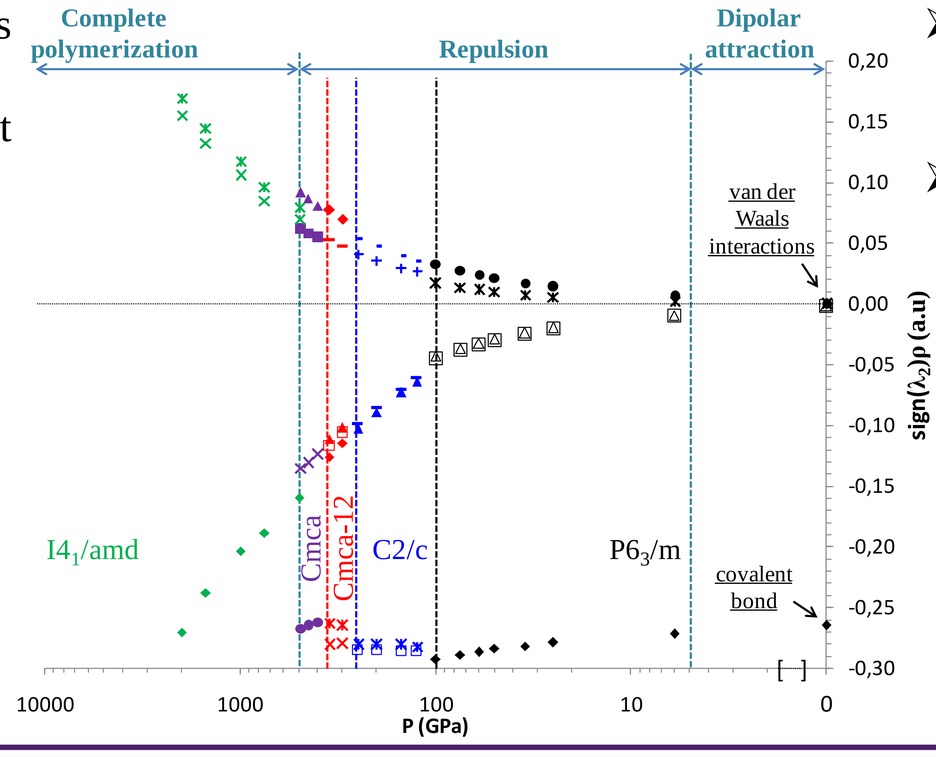
Dipolar attraction for $r_s \geq 1.58$:
- only weak vdW interactions (ρ = 0 to 0.006 a.u.)
- $V(\lambda_2 < 0)$ increase and reach its maxima at $r_s = 1.58$
- this is correlated with the strengthening of the vdW interactions

Repulsion for $1.58 < r_s < 0.88$:
- the intermolecular interactions strengthen and the covalent bonds become weaker under pressure.
- $V(\lambda_2 < 0)$ decreases which is correlated with the fact that the vdW interactions progressively transform into covalent bonds.
- $V(\lambda_2 > 0)$ continues to increase up to $r_s = 0.99$ and then decreases

Complete polymerization for $r_s \leq 0.88$:
- the NCI peaks 1 and 2 are superposed
- the interactions 1 and 2 become equivalent
- the model system has polymerized

Best candidates

- In dense hydrogen; each H_2 molecule or hydrogen interacts mainly with the nearest neighbors
- Our analyses focuses on the solid phases using the first coordination spheres of each non-equivalent hydrogen.



- similar to profile of the $3H_2$ molecular model.
- possibility of delimiting this profile in three regions already identified in the section « $3H_2$ molecular model ». For this, the equalization index values correlating $r_s(3H_2)$ and P can be used (results not shown here).

*s(ρ) = 0.2 a.u. ;
color scale: -0.2 < sign(λ_2)ρ < 0.05 a.u.
**s(ρ) = 0.1 a.u. ;
color scale: -0.2 < sign(λ_2)ρ < 0.2 a.u.

Conclusion

- H_2 solid phases and the polymerization process can be understood thanks to the $3H_2$ molecular model.
- Three transition regimes were highlighted: dipolar attraction, repulsion and complete polymerization.
- The polymerization process starts in the repulsive region.
- The NCI topological tool is therefore a very useful tool for the analysis of bonding transformation.