

Endohedral confinement of molecular hydrogen

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Abstract

Molecular hydrogen endohedrally confined using H_{2n} -fullerene-like cavities is investigated with resort to density functional theory. Firstly, the pressure dependence of the ground state energy and internuclear distance of a single H_2 molecule is obtained as a function of a H_{20} cage volume. Secondly, 30 hydrogen atoms are allowed to relax under the confinement of a H_{60} cage of radius $R \sim 4 \text{ \AA}$ to reach a configuration of minimum energy. Hydrogen molecules form and self-assemble into a $(H_2)_{15}$ stable cluster characterized by two coaxial sixfold symmetry ring structures. The present confinement model gives results in agreement with experimental observations.

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1. Introduction

In the course of investigations of hydrogen under pressure, spherical and spheroidal hard- and soft-wall cage models have been used to study pressure-effects on the electronic and structural properties of the H atom [1], the H_2 molecule and ions [2–8]. Reasonable qualitative and semi-quantitative agreement has been found with experiments of compressed H_2 in Ne matrices [9] and with studies of isochoric molecular dissociation in dense hydrogen [10]. The general conclusion is that cage models may be useful to study compression effects on H and H_2 properties provided more realistic confining potentials are used. Indeed, cage models alone cannot account for all properties of solid hydrogen under compression due to the important coupling between electronic properties of the host medium and those of the caged-in molecules [9]. However, an adequate means to account for this aspect is the use of cage models concomitant with solid properties [11].

In contrast with previous treatments, in this communication we consider a more realistic confinement

model of molecular hydrogen based on endohedral H_{20} and H_{60} fullerene-like cages. Clearly, the aforementioned structures do not exist in nature but, we shall use them as cage models to simulate the pressure effects on the molecular objects located in the cage. The model is first applied to a single hydrogen molecule inside an H_{20} cage of varying mean radius. The behavior of the molecular ground-state energy and geometry as a function of cage size is reported and compared to previous theoretical studies based on less realistic confining conditions. The static cold pressure associated to changes in molecular-energy as a function of cage volume is also obtained. Some pressure-dependent local properties such as H–H internuclear distance and ground-state energy compare favorably to sophisticated Quantum Monte Carlo (QMC) calculations [12] and experimental measurements related to solid hydrogen with a hcp crystalline structure [13]. The reader should be aware that, the model we present is based on localized orbitals and the boundary conditions are those imposed by the confining cage, hence local properties can only be studied. In contrast, the QMC model is based on delocalized electrons, considers periodic boundary conditions and allows the study of bulk properties.

As a second application of the model, 30 H atoms are confined within a H_{60} fullerene-like cage of radius $R \sim 4 \text{ \AA}$. The lowest-energy structure results in the formation

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of a self-assembled $(\text{H}_2)_{15}$ cluster. The formation and characterization of this self-assembled cluster under confinement is reported for the first time.

2. Method

Given the nature of the models, the computations are done using the density functional theory (DFT) formalism for molecules. We have resort to gaussian basis sets of double-zeta quality with polarization effects included in the valence electrons. In the literature they are recognized as DZVP basis sets. Such sets have been optimized to be used specially in the DFT approach and substantially minimize superposition errors. Gradient corrections of the Becke and Lee-Yang-Parr types are incorporated into the exchange and correlation energies, respectively, to account for inhomogeneities of the electron density [14,15]. The eigenvalue problem is solved through a self-consistent field process. Fine grids are used in the numerical integrations with tight convergence criteria. Regardless of the molecular composition, the integration scheme ensures a total energy accuracy of $\sim 10^{-7}$ a.u. The importance of zero-point vibrational energies (ZPVE) for confined systems has been emphasized by several authors [12,16]. In view of the high computational cost, the determination of the ZPVE was restricted to that of the H_2 molecule. In this case, the computation of the ZPVE of the *supermolecule* conformed by the enclosed molecule and the cage is obtained by summing the harmonic frequencies. However, a detailed analysis of the frequency spectrum allows to separate the vibrational modes associated to the molecule alone. For the highest frequency mode, it was found that-independently of the cage radius- every atom of the cage is at rest and the molecule vibrates on a stretching mode. Therefore, the highest vibration frequency was taken into account to calculate the ZPVE of the confined molecule.

3. Results and discussion

3.1. Hydrogen molecule

For a single H_2 molecule, the ground state electronic energy and structural behavior under pressure is determined by changing the cage size defined by its mean radius, $R = N^{-1} \sum_{i=1}^N r_i$, where N is the number of H-atoms forming the cage and r_i the radial distance to atom ' i ' measured from the origin. For each radius, the energy associated to the H_2 molecule is $E(\text{H}_2) = E(\text{H}_{22}) - E(\text{H}_{20})$ with $E(\text{H}_{22})$ the total *supermolecule* energy and $E(\text{H}_{20})$ the cage energy. Fig. 1 shows the H_2 energy dependence with volume obtained in this work as compared to QMC calculations [12] and calculations

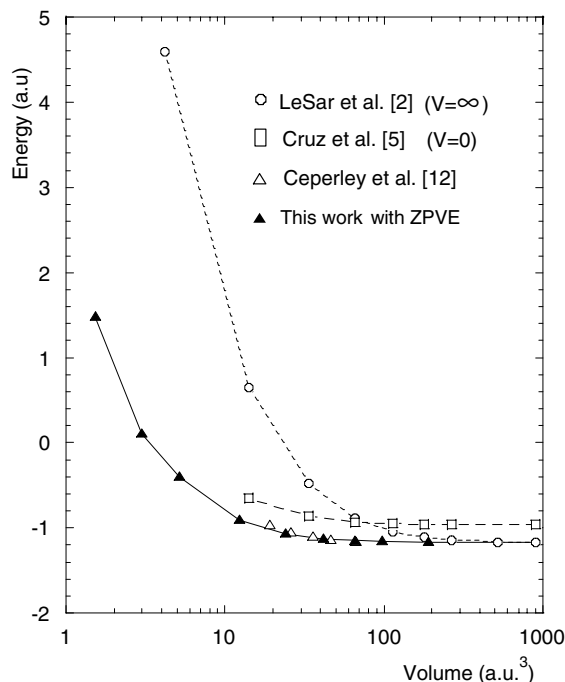


Fig. 1. Total energy of an H_2 molecule as a function of confinement volume. Open circles: variational calculation using a five-term James–Coolidge trial wave function and spheroidal boxes with rigid walls ($V = \infty$). Open squares: variational calculation using a single-spherical gaussian orbital representation and spherical boxes with walls of barrier height $V = 0$. Open triangles: Quantum Monte Carlo calculations in the molecular phase of solid hydrogen. Solid triangles: results of this work. Lines are drawn to guide the eye.

based on rigid [2] and soft [5] cage models. The ZPVE of the H_2 molecule is included in Fig. 1. While a very good agreement with the QMC results is observed, the exaggerated prediction of the energy-volume ($E-V$) behavior by the rigid cage model is apparent from this figure. Interestingly, the trend of the $E-V$ curve obtained from the soft spherical cage model is in good qualitative agreement with this work and the QMC calculations. The quantitative difference is due to the use of a single floating spherical gaussian orbital (FSGO) for H_2 in [5], which only yields $\sim 80\%$ of the Hartree–Fock energy.

Changes in total energy as a function of molecular volume yield the pressure as $P = -\partial E/\partial V$, where V is calculated considering the electronic density of the shell atoms and that of the enclosed object equally sharing the space in between (because all atoms are of the same species). Accordingly, the effective molecular radius associated to H_2 is $R/2$. The pressure was calculated after constructing an interpolating $E-V$ curve among various energy calculations for specific volumes and then taking its derivative at the volume of interest. For pressure estimates at arbitrary volumes, a Vinet [17] curve was fitted to our $P-V$ values taking the zero-pressure reference volume of $23 \text{ cm}^3/\text{mol}$ [18]. The fitting procedure

yields an equivalent ‘bulk modulus’ and its pressure derivative equal to $K_0 = 0.1544$ GPa and $K'_0 = 7.1664$.

The variation with pressure of the H_2 internuclear distance is shown in Fig. 2. We include measurements from Ulivi et al. [13] for a pressure range from 0.3 to 20 GPa. Corresponding predictions from the rigid and soft cage models are also shown for comparison. The reasonable agreement between the results of this work – obtained at $T = 0$ K – and the experimental ones obtained at $T = 300$ K suggests that bond contraction is almost temperature independent, for the pressure range considered, in qualitative agreement with a previous work by Magro et al. [19]. Furthermore, the better agreement with experiment obtained in this work as compared to previous predictions based on cage models is related to a more realistic description of the confining wall and to an improved quantum mechanical calculation. For instance, as pressure increases, the soft cage model $V = 0$ from [5] predicts a stronger bond-length contraction as compared to the results of this work (see Fig. 2). This different behavior is due to a larger screening of the proton-proton interaction from a buildup of electronic charge in the bond region as implied by the single-FSGO representation, whereas in the present calculation screening is lower due to a more realistic electronic charge density distribution around nuclei and the bond region.

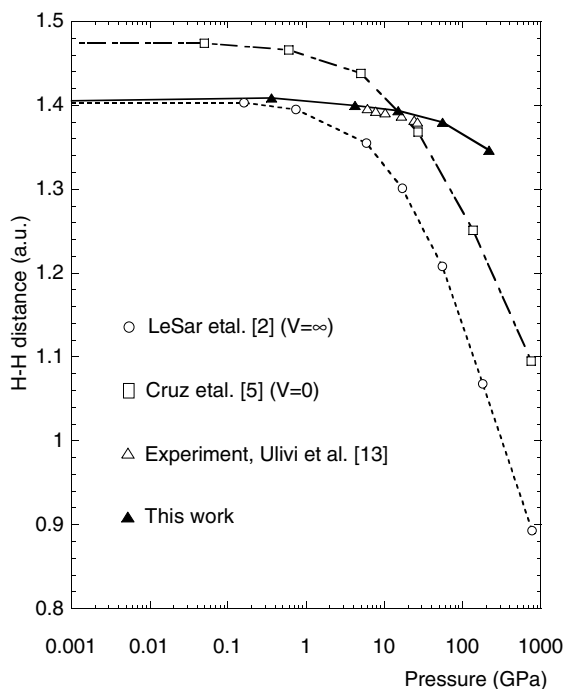


Fig. 2. Variation of the H–H internuclear distance with pressure. Open circles: results from the rigid-wall spheroidal box model. Open squares: results from the soft-wall spherical box model. Open triangles: experimental results from pure rotational Raman scattering in fluid and solid hydrogen at 300 K. Solid triangles: results from this work. Lines are drawn to guide the eye.

3.2. Formation of an $(H_2)_{15}$ molecular cluster under confinement

The recent observation of small molecular hydrogen clusters in clathrate hydrate cages after static compression of a mixture of H_2/H_2O [20] has motivated us to explore the effect of endohedral confinement on the properties of H_2 clusters using our model with a H_{60} cage. To this end, similar DFT calculations as before were carried out as follows. Initially 30 H atoms were randomly located and allowed to evolve energetically inside a static H_{60} fullerene-like cage of mean radius $R \approx 4$ Å until the lowest energy structure (LES) configuration was achieved. The cluster energy (-16.8971 a.u.) was obtained as $E[(H_2)_{15}] = E(H_{90}) - E(H_{60})$, with $E(H_{90})$ and $E(H_{60})$ the total *supermolecule* energy and cage energy, respectively. It was found that the hydrogens self-assemble into an ordered array of 15 H_2 molecules (Fig. 3), where twelve of them have their centers located at the vertices of two staggered parallel hexagonal planes, plus a central molecule between planes (bond length 0.73 Å), in an almost perpendicular position relative to the planes, and a top and a bottom centered molecule (bond length 0.73 Å) with molecular axis parallel to each plane. The bond length and mean distance between centers of mass (CM) of H_2 molecules in the top (bottom) hexagonal ring are 0.73 (0.74 Å) and 2.02 ± 0.01 (1.95 ± 0.04 Å), respectively. The polar angles ϑ formed by the molecular axes relative to the normal of the planes lie in the range $45^\circ \leq \vartheta \leq 62^\circ$, while the in-plane azimuthal angles φ , measured from the line joining the nearest molecule in the plane, fall in the range $3^\circ \leq \varphi \leq 26^\circ$. The top and bottom molecules show symmetric orientations with respect to their closest hexagonal planes (Fig. 3). While the shift angle observed between hexagonal planes is attributed to a coulombic repulsion, due to the close distance of planes induced by the confining cage, the differences observed in the ϑ and also in the φ angles suggest the presence of anisotropies due to the interplay of interactions among molecules of the cluster and with the cage atoms. This effect is also assumed to be responsible for the small differences observed in bond lengths and CM distances. Still, a self-assembling behavior of the system into a high symmetry characterized by a rotation axis of order 6 is evident. A crude estimate of the pressure associated to this system yields ~ 39 GPa, which is obtained from our Vinet equation by taking the effective cluster radius as: $R_{\text{cluster}} = (N_m - 1)^{-1} \sum_{j=1}^{N_m-1} [R_j^{\text{CM}} + (R - R_j^{\text{CM}})/2]$, with R_j^{CM} the radial distance from the origin to the CM of molecule ‘ j ’ and $N_m - 1$ the number of molecules in the cluster excluding the one at the origin.

To conclude, cage models with realistic confining potentials combined with a high-level DFT treatment may provide important information on compression effects on the properties of molecular hydrogen. The

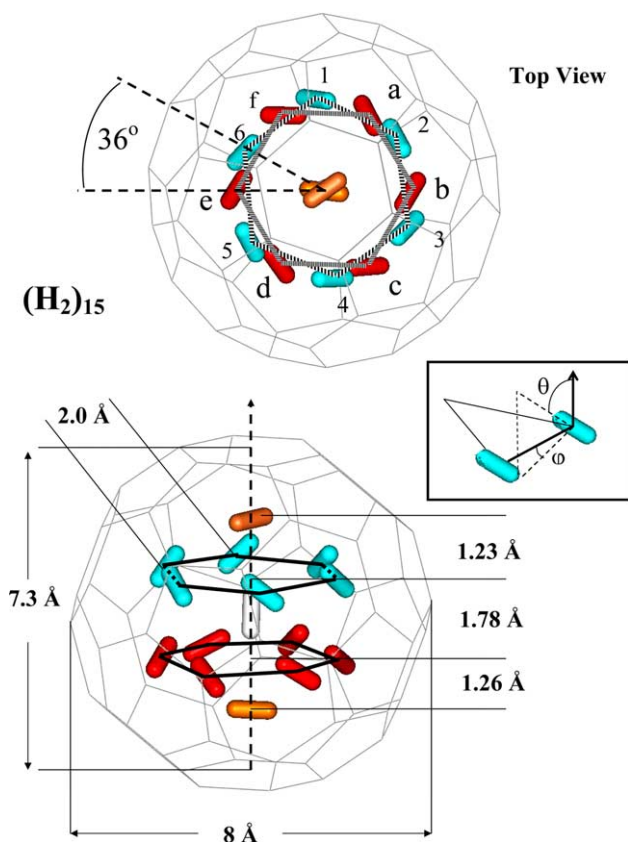


Fig. 3. Structure of a self-assembled $(\text{H}_2)_{15}$ cluster inside a H_{60} fullerene-like cage of mean radius $R \approx 4 \text{ \AA}$. Two coaxial rings of hexagonal symmetry formed by molecular centers (1–6) and (a–f) around an axis defined by three H_2 molecules are observed. The top view shows a shift angle of 36° between hexagonal planes while the lateral view displays some characteristic distances. The inset indicates the polar (θ) and in-plane azimuthal (ϕ) angles formed by the molecular axes (see text).

model predicts a dependence of the bond length upon pressure in agreement with the experiments, and with more sophisticated calculations for the evolution of the ground-state energy. The formation of a stable self-assembled structure of a $(\text{H}_2)_{15}$ clusters under confinement is reported for the first time as a result of this study. Indeed, proper account of zero-point-energy effects as well as the survey of thermal effects on cluster

stability would enhance the prediction capability of the model. These aspects are currently under study and will be reported elsewhere.

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References

- [1] E. Ley-Koo, S. Rubinstein, *J. Chem. Phys.* 71 (1979) 351.
- [2] R. LeSar, D.R. Herschbach, *J. Phys. Chem.* 85 (1981) 2798; *J. Phys. Chem.* 87 (1983) 5202.
- [3] E. Ley-Koo, S.A. Cruz, *J. Chem. Phys.* 74 (1981) 4603.
- [4] T. Pang, *Phys. Rev. A* 49 (1994) 1709.
- [5] S.A. Cruz, J. Soullard, E.G. Gamaly, *Phys. Rev. A* 60 (1999) 2207.
- [6] T. Sako, G.H.F. Diercksen, *J. Phys.: Condens. Matter* 15 (2003) 5487.
- [7] T. Sako, G.H.F. Diercksen, *J. Phys. B: At. Mol. Opt. Phys.* 36 (2003) 3743.
- [8] T. Sako, G.H.F. Diercksen, *J. Phys. B: At. Mol. Opt. Phys.* 36 (2003) 1681.
- [9] P. Loubeyre, R. Letoullec, J.P. Pinceaux, *Phys. Rev. Lett.* 67 (1991) 3271.
- [10] N.H. March, M.P. Tosi, *Nuovo Cimento D* 18 (1996) 1061.
- [11] S. Chakravarty, J.H. Rose, D. Wood, N.W. Ashcroft, *Phys. Rev. B* 24 (1981) 1624.
- [12] D.M. Ceperley, B.J. Alder, *Phys. Rev. B* 36 (1987) 2092.
- [13] L. Ulivi, M. Zoppi, L. Gioe, G. Pratesi, *Phys. Rev. B* 58 (1998) 2383.
- [14] K.A. Johnson, N.W. Ashcroft, *Nature* 403 (2000) 632.
- [15] R.J. Harrison, et al. NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.1, Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA, 2002.
- [16] T. Takezawa, H. Nagara, K. Nagao, *J. Phys.: Condens. Matter* 14 (2002) 10411.
- [17] P. Vinet, J.H. Rose, J. Ferrante, J.R. Smith, *J. Phys.: Condens. Matter* 1 (1989) 1941.
- [18] R.J. Hemley, Ho-kwang Mao, *J. Low Temp. Phys.* 122 (2001) 331.
- [19] W.R. Magro, D.M. Ceperley, C. Pierleoni, B. Bernu, *Phys. Rev. Lett.* 76 (1996) 1240.
- [20] W.L. Mao et al., *Science* 297 (2002) 2247.