Dense molecular hydrogen: A comment on Nat. Commun. 11, 6334

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Abstract

Using dimensional analysis, possible reasons are discussed why the pressure-induced spin bi-stability in dense molecular hydrogen occurs at an intermolecular distance of 1.509(14) Å and why the intramolecular distance levels off at 0.727(5) Å at high pressures.

Keywords: Spin coupling crossover, dense molecular hydrogen, magnetic self-energy, characteristic magnetic length, dipolar interactions, high pressure NMR spectroscopy

Proton nuclear magnetic resonance data of solid molecular hydrogen (H_2) at room temperature indicated a pressure induced spin-crossover from a spin I=1 quadrupole system to a spin I=1/2 dipole system [1]. Above a characteristic pressure (70 GPa), spectral features became apparent that are typical for a homo-nuclear (like spins) dipole-dipole coupling between nearest and second nearest neighbours, that is, a superposition of two dipolar powder spectra (Pake patterns) was observed. A Pake line shape results from closely spaced, approximately isolated spin pairs that are distributed at all angles in a powder sample and whose Zeeman levels are perturbed by a classical dipolar interaction parametrized by an inverse cubic dependence on the atomic distance. The experiment of Meier et al. 2020 suggests that at pressures greater than 70 GPa free molecular rotation can no longer be assumed.

By analysing the NMR spectra for such a mixed case, Meier et al. 2020 determined the values for the nearest distance (r_n) and second nearest distance (r_{nn}) as a function of pressure. The authors obtained $r_{nn} = 1.509(14)$ Å at the spin bi-stability and $r_n = 0.727(5)$ Å at the highest pressure. For every distance (r) between two nuclear magnetic moments of the proton (μ_p) the magnetic energy $\mathcal{E}_m(r) \equiv \mu_0/(4\pi)\ \mu_p^2\ r^{-3}$ can be calculated, which is related to the static dipolar-dipolar coupling constant υ_d in the unit Hz according to $\upsilon_d = 4\mathcal{E}_m(r)/h$. The factor 4 is due to the spin I=1/2. In the homo-nuclear case, the separation between the inner peaks of the Pake doublet is $(3/2)\upsilon_d$.

At atmospheric pressure and 1 K, the molar volume of solid molecular hydrogen is ≈23 cm^3/mole [2], that is, about 39 $Å^3$ per molecule indicating that the H_2 molecules are far apart (≈3.79 Å) compared to their proton-proton separation (bond length) of ≈0.741 Å in the gas phase [3]. At low pressure, hydrogen is extremely compressible. As the pressure increases, the molecular integrity remains unaltered, that is, the bond length remains roughly constant, whereas the van der Waals (dipole-dipole) space is easily compressed till the molecules are penetrating the repulsive region of the intermolecular interaction. At a certain pressure, the intramolecular separation must attain a minimum value because the covalent bond is energetically too costly to contract any further. In the repulsive region of the intermolecular interaction solid hydrogen can presumably be regarded as H_2 molecules differing in their orientations.

Due to various arguments [4], this author axiomatically introduced a system of units based on the unit relationship $kg=ms^2$. With the speed of light c, the unit second can be expressed in the unit meter according to $s=m/c$. It follows that $kg=m^3/c^2$, $Joule=m^3$ and $Coulomb=m^2(4\pi\varepsilon_0)^{1/2}$. These transformations cause units to become powers of the meter. Such a transformation can also be performed for the unit of the magnetic moment Am^2. In this case, the unit relation $Am^2=m^3(4\pi\varepsilon_0)^{1/2}c$ applies.

The intrinsic nuclear magnetic moment of the proton is $\approx 1.41\ 10^{-26}$ Am^2. If this value is divided by the factor $(4\pi\varepsilon_0)^{1/2}c$, the result is $\approx 4.46\ 10^{-30}$ m^3 or $(\approx 1.646$ Å$)^3$ if the space is isotropic. In this view, ≈ 1.646 Å is a characteristic magnetic length (r_{mag_proton}), or $\approx 4.46\ 10^{-30}$ J is a characteristic magnetic energy ($\mathcal{E}_{self\_proton}$) of the proton's magnetic moment basically meaning that the intrinsic magnetic moment is localized over a finite region of space and repels other objects from being in this place. For comparison, the elementary Bohr magneton μ_B in the unit m^3 is $(1/2)(h_{bar}c)^{1/2}\alpha^{1/2}\lambda_{e\_bar}$ or $(\approx 1.431\ nm)^3$. It is easy to show that by definition $\mathcal{E}_{self}$ equals $\mathcal{E}_m(r_{mag})$ for any magnetic moment μ.

If the value $\mathcal{E}_m(r_{nn})$ with $r_{nn}=1.509(14)$ Å at the spin crossover is compared with $\mathcal{E}_{self\_proton}$ determined by dimensional analysis, the ansatz $\mathcal{E}_m(r_{nn})=\lambda\mathcal{E}_{self\_proton}$ experimentally yields $\lambda(r_{nn})=1.30(4)$, which roughly corresponds to $(3/5)^{-1/2}$ or ≈ 1.29. As a comparison, the self-energy $\mathcal{E}_{Coulomb}$, that is, the energy, that is necessary to build up a simple sphere with radius r and total charge Q, is $(3/5)Q^2(4\pi\varepsilon_0 r)^{-1}$. Unfortunately, the error in r_{nn} is too large to decide with certainty which critical dimensionless property of the local environment (interspace) affects the interaction between H_2 molecules and hence codifies the heuristic proportionality factor $\lambda(r)$. In any case, there must be a fundamental reason, why spin-addition inside the H_2 molecule breaks down below a critical intermolecular H-H distance as experimental evidence clearly indicates, or to put it another way, why molecular hydrogen appears to represent an isolated, undistorted system only above a critical intermolecular H-H distance. It is hypothesised that the numerical value $(3/5)^{-1/2}$ is associated with the molecular rotation of the H_2 molecule.

By analogy, the same empirical considerations as for r_{nn} can be made in the case of molecular pairing, that is, for the nearest distance $r_n=0.727(5)$ Å at the highest pressure (123 GPa). The analogy yields for the constant of proportionality $\lambda(r_n)=11.60(25)$, which interestingly corresponds to $\alpha^{-1/2}$ or ≈ 11.71 respectively. It is unclear why $\lambda(r_n)$ lies close to the inverse square root of the fine structure constant α, which is directly proportional to the elementary charge squared. More experimental data at higher pressures are necessary to clarify whether the nearest distance r_n attains a critical value, as suspected.

References

[1] Nuclear spin coupling crossover in dense molecular hydrogen
T Meier et al Nat Commun **11** 6334 (2020)

[2] The solid molecular hydrogens in the condensed phase: Fundamentals and static properties
IF Silvera Rev Mod Phys **52** 393 (1980)

[3] Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules
KP Huber and G Herzberg, Van Nostrand Reinhold Company (1979)

[4] On the Origin of Natural Constants
Hans Peter Good, De Gruyter Berlin (2018)