Chemistry Research Journal, **2016, 1(5):9-10**

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

An unusual approach to the bond enthalpy in hydrogen molecule: the contribution of relativistic effects

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Abstract In the present work, the H-H bond enthalpy in hydrogen molecule explained/calculated by using the Bohr atom approach, as well as Slater rules and taking into account relativistic effects. It is shown that in the hydrogen molecule, the electron moves at 0.7155 c, with a relativistic mass of 13.04 x 10^{-31} kg and that the most part of the H-H bond enthalpy are related with the change in potential energy in individual H atoms.

Keywords Hydrogen; Bond enthalpy; Relativity; Slater rules; Bohr atom**.**

Introduction

Traditionally, relativistic effects in atoms are considered as relevant only to heavy elements, that is, those with high Z values, such as gold and mercury [1]. The H-H bond in hydrogen molecule it is a classic example of covalent bond, with the H-H bond viewed as consequence of the sharing of an electron pair by the hydrogen atoms. Such view is present in the early proposals of Lewis, as well on most modern and sophisticated models of the chemical bond, such as valence bond theory or molecular orbital theory. It is considered that the H-H bond cannot be ionic, since the attractive force between the H^+ and H^{-1} ions cannot provide enough energy in order to compensate the energy consumed to form the ions. In the present work, an unusual approach is employed in order to explain the H-H bond enthalpy in hydrogen molecule: a combination of Bohr atomic model and some equations of special relativity.

Calculations, Results and Discussions

The Bohr radius is equal 52,9 pm. So, the H-H bond length, that is, the distance from one hydrogen nucleus to the other in hydrogen molecule, could be, in a first moment, considered as 52.9 x 2 = 105.8 pm. However, the experimental H-H bond length it is of 74 pm. So, if one imagine the hydrogen molecule as two hydrogen atoms side by side, the radius (the distance from the proton to its electron) in the bonded hydrogen atom can be calculated as 74/2 = 37 pm.

From the special theory of relativity, we have:

$$L' = L\ [1-(v^2/c^2)]^{1/2}$$

the equation that correlates the contraction of a body travelling at speeds closer to the speed of light. An analogous equation is:

$$a_{rel} = a_o\ [1-(v^2/c^2)]^{1/2}$$

such equation allows the calculation of the relativistic radius of an electron travelling at speed *v*.

Taking the a_o value and the value of a_{rel}= 37 pm, respectively, to the free and bonded hydrogen atom, the obtained *v* value is 0.7155 c. That is, in the hydrogen molecule, the electron moves at almost 72% of the light speed. Certainly, a not negligible value. For comparison, in a free hydrogen atom, the electron moves at ~(1/137) c.

Such result seems quite reasonable: as the electron approach the nucleus, its radial velocity increases.

Taking the calculated *v* value, the relativistic mass of the electron in the bonded hydrogen atom can be calculated by

$$m_{rel}= m_e /[1-(v^2/c^2)]^{1/2}$$

as equal 13.04 x 10^{-31}kg (the rest mass, m_e is 9.11 x 10^{-31} kg).

In the Bohr atom, the electron energy can be calculated by:

$$E = -(m_e q_e^4)/8h^2\varepsilon_o^2)$$

Such equation provides a value of -1,313.56 kJmol^{-1} (13.61 eV) to the electron in the free hydrogen atom.

If we repeat the calculation using, in the previous equation, the calculated relativistic mass, we obtain -1,881.79 kJ mol^{-1}. That is, a difference of 568.23 kJ mol^{-1}.

Since in hydrogen molecule there are two hydrogen atoms: 2 x (568.23) = 1,136.46 kJ mol^{-1}. However, the H-H bond enthalpy is equal 432.01 kJ mol^{-1}[2]. So, there is a difference of700.46 kJ mol^{-1} to be explained. Such difference is due to the proton-proton repulsion.

Using Coulomb´s law, the 700.46 kJ mol^{-1} value,and taking a 74 pm bond length, it is possible to calculate the charge of each proton as 9.81 x 10^{-20} Coulomb. That is, 0.61e. So, each proton is “feeling” only 61% of each other charge. Such fact could be seen as predictable, taking into account the shielding effect exerted by the two electrons.

In comparison with the free atom, each bonded hydrogen has an “extra” electron. Since the effective nuclear charge is 0.61, the screening (or shielding) factor is 1-0.61 = 0.39. Such value is in good agreement with Slater rules [3] that establish a 0.35 value to the shielding constant for electrons located at the same energy level. The 0.04 difference could be attributed to the most efficient shielding capacity of the electrons closer to the nucleus (bonded H atom *versus* free H atom).

Despite the fact that the concepts of nuclear effective charge and shielding factor were proposed by Slater thinking in isolated atoms, it seems that it works quite well for bonded atoms too.

The obtained results shows that even to the lightest element, the relativistic effects are prominent, once chemical bonds are formed.

It can be also concluded that the most part of the hydrogen bond enthalpy comes from the change in the potential energy of individual hydrogen atoms, not from a potential energy “of the molecule”.

Since bond enthalpies are related with orbitals energy levels, such effects are, of course, expected to be extensible to spectroscopic properties, etc.

References

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