USING MOLECULAR MODELLING TO STUDY BOND DISSOCIATION ENERGY: METHANE AS A STUDY CASE

Robson Fernandes de Farias
Universidade Federal do Rio Grande do Norte, Cx. Postal 1664, 59078-970, Natal-RN, Brasil.
Email: robdefarias@yahoo.com.br

ABSTRACT

The present work describes how molecular modelling (DFT approach) can be used to calculated the H_3C-H bond dissociation energy, in a didactical approach that can be employed in both, undergraduate or graduation courses. *[African Journal of Chemical Education—AJCE 9(2), July 2019]*

INTRODUCTION

In chemistry, the bond dissociation energy is a key parameter. It could be associated, for example, with the exothermic or endothermic nature of a given reaction, as well as with the higher or lower reactivity of a given compound.

In the present work it is shown how molecular modelling can be employed to "measure", with great accuracy, bond dissociation energy values, using methane as example.

This approach can be used in both, undergraduate or graduation courses.

METHODOLOGY

Methane was modelled by using DFT (M06-2X; 6-311 + G**) approach. The obtained results (electrostatic charges on carbon and hydrogen and vibrational modes) were employed to calculate the C-H bond dissociation energy in H_3C-H. The obtained result was compared with those from literature [1].

RESULTS AND DISCUSSION

The H_3C-H bond dissociation energy value employed here as reference is that from CRC Handbook [1]: 439.3 ± 0.4 kJmol^{-1}.

Then, the same bond dissociation energy was calculated by using the data obtained by molecular modelling: the electrostatic charge on carbon and hydrogen, respectively: -0.935e and + 0.233e, as well as the energy associated with the stretching vibrational modes.

Since $e^2/4\pi\varepsilon_o = 2.3071$ x 10^{-28} J.m, using the calculated electrostatic charges (as well as the calculated bond distance: 108.9 pm), and assuming that the ionic component of the bond energy can be calculated by Coulomb´s law, a value of 277.83 kJmol^{-1} is calculated.

Hence, the second part is to calculate the covalent contribution for the bond energy. The calculated infrared spectrum for methane is shown in Figure 1.
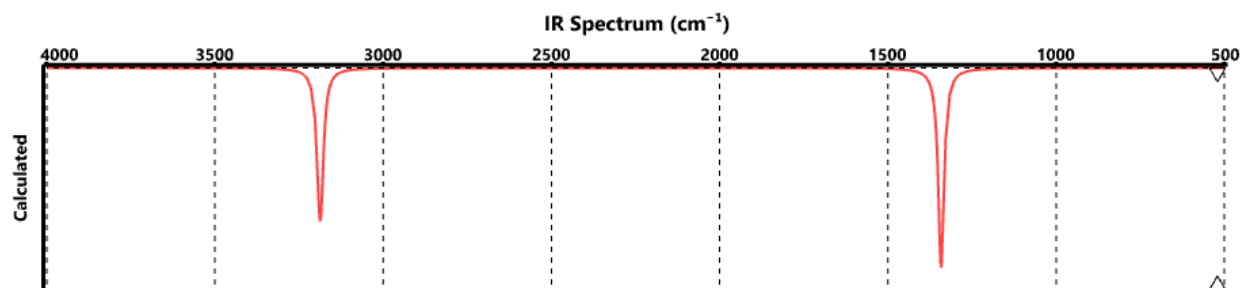

Fig. 1. Calculated infrared spectrum for methane.

In such spectrum, only the two most intense bands can be seen. However, a complete set of vibration bands is provided by the calculation: 3190, 3187, 3183, 3070, 1566, 1565, 1343, 1342 and 1341 cm^{-1}. From those vibration bands, only those at 3190, 3187 (this bands, despite its proximity, are indeed due to two distinct vibration modes; in Figure 1 they are, of course, superimposed), 3183 and 3070 cm^{-1} are associates with stretching modes (the other ones are associates with bending, rocking, etc., vibrational modes). Hence, only these four bands will be employed to calculate the covalent contribution to the bond energy. Such choice is due to the fact that only the stretching of the chemical bond can be directly associated with the bond constant force and hence with the bond dissociation energy [2].

Since $1 cm^{-1} = 0.0119627$ $kJmol^{-1}$ [1], to the four considered infrared bands we can calculate the following values: 38.16, 38.13, 38.08 and 36.73 $kJmol^{-1}$, respectively, and a total of 151.10 $kJmol^{-1}$.

Hence, a total value of $277.83 + 151.10 = 428.93$ $kJmol^{-1}$ for the H_3C-H bond dissociation energy can be calculated, in excellent agreement (-2.4 %) with the reference value.

A very important (and maybe surprisingly to the undergraduate student) fact must be pointed out: as can be verified, the ionic contribution is larger than the covalent contribution in the C-H bond in methane.

REFERENCES

1. CRC Handbook of Chemistry and Physics 96th ed., Taylor and Francis, Boca Raton, 2016.
2. D. Cremer, A. Wu, A. Larsson, E. Kraka, Some Thoughts about Bond Energies, Bond Lengths, and Force Constants, *J. Mol. Model*. 6 (2000) 396.