



A novel method for the calculation of bond stretching force constants of diatomic molecules



Savaş Kaya^{a,*}, Cemal Kaya^a, I.B. Obot^b, Nazmul Islam^c

^a Cumhuriyet University, Science Faculty, Department of Chemistry, 58140 Sivas/Turkey

^b Centre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

^c Department of Basic Science & Humanities/Chemistry, Techno India-Balurghat (formerly Techno Global-Balurghat), Balurghat 733103, India

ARTICLE INFO

Article history:

Received 24 June 2015

Received in revised form 2 October 2015

Accepted 22 October 2015

Available online 24 October 2015

Keywords:

Chemical hardness

Bond length

Bond force constant

DFT

A new molecular hardness equation

ABSTRACT

Chemical hardness is one of the chemical reactivity descriptors of chemical species and this concept has widely benefited from the development of Density Functional Theory (DFT). In the present report, chemical hardness values for approximately fifty diatomic molecules have been calculated using a new molecular hardness (η_M) equation derived by us in recent times. Then, correlation between force constant (k) and chemical hardness for the above mentioned diatomic molecules that situate hydrides, halides, oxides and sulfides among them has been investigated. Consequently, a relation that can be presented by a simple equation between chemical hardness with bond stretching force constants has been found.

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1. Introduction

A primary goal of theoretical chemists is to predict the structure, stability, and chemical reactivity of molecules that are difficult to investigate by experimental means. Several models based on simplifications and assumptions, are available to provide new insights into the properties of molecules. It is unfortunate that the atoms and molecules are invisible only we can observe some radiation signals coming out the atom and molecule. The signals bear the signature of all the energetic effects including the effects of relativity present in the complex electronic structure of the species. The electron correlation, relaxation and relativity are the actual features of the inner plenum of electron constitution of atom and molecule. The actual features of the plenum of electron constitution are incorporated into the signals coming out of inner world of the atoms. Ghosh and Islam [1,2] rightly pointed out that any calculation of atomic property entailing spectroscopic data, the electron correlation, relaxation and relativity are automatically subsumed in such calculated property.

The present exercise investigates force constants in diatomic molecules, a measure of the stiffness of the bond. Bond stretching force constants of diatomic molecules are generally used to predict equilibrium geometries, electron correlation or basis set effects and harmonic vibrational frequencies of the molecules. Bond stretching force constants also have important applications in vibrational spectroscopy (IR and Raman

spectroscopies) and in molecular mechanics force fields. If a bond is distorted (stretched or contracted) from its equilibrium length, the molecule's energy increases and, as a result, there is a force on each atom in the direction that reduces the bond energy. Stronger the bond, larger will be the force constant. Thus the force constant is linearly related to bond order. Bond force constants of molecules can be easily determined by means of the data of IR or Raman spectroscopy [3,4]. Using these spectroscopic methods, bond vibrational frequencies of molecules are easily determined and for diatomic molecules, considering the following equation, bond force constants of diatomic molecules are calculated [5].

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1)$$

where c , k and μ are light speed, bond force constant and reduced mass, respectively.

Conceptual Density Functional Theory (CDFT) [6,7] provides great conveniences to chemists for understanding of chemical reactivity. Chemical reactivity descriptors such as chemical hardness (η) [8–11], chemical potential (μ) [12] and electronegativity (χ) [13,14] are defined as the derivatives of the electronic energy (E) of a system with respect to number of electrons (N) at a constant external potential, $v(r)$ and can be calculated considering ionization energy (I) and electron affinity (A) values of chemical species through the contributions to quantum

* Corresponding author.

E-mail address: savaskaya@cumhuriyet.edu.tr (S. Kaya).

chemistry of this theory [15].

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \quad (2)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} \quad (3)$$

Pearson and Parr put forward the operational definitions of chemical hardness, chemical potential and electronegativity as follows by applying the finite differences approximation to Eq. (2) and Eq. (3) [16,17].

$$-\mu = \chi = \frac{I + A}{2} \quad (4)$$

$$\eta = I - A \quad (5)$$

where I is the ionization energy and A is the electron affinity of the chemical species.

In recent times, a new and useful method for calculation of chemical hardness of molecules (η_M) has been presented by us [18].

$$\eta_M = \frac{2 \sum_{i=1}^N \frac{b_i}{a_i} + q_M}{\sum_{i=1}^N \frac{1}{a_i}} \quad (6)$$

In this equation, q_M is the charge of molecule, N is the number of atoms in molecule, and a_i and b_i are the correlation parameters. These correlation parameters are defined as:

$$a_i = \frac{I + A}{2} \quad (7)$$

$$b_i = \frac{I - A}{2} \quad (8)$$

Badger [19] put forwarded the empirical relation between bond lengths, force constants and bond dissociation energies as:

$$k = \frac{1.86 \times 10^5}{(r_e - d_{ij})^3} \quad (9)$$

where, k is bond stretching force constant in dyn cm^{-1} units. r_e represents the internuclear distance in Angstrom (\AA) units and d_{ij} is a function of the position of bonded atoms in the periodic table.

A relation between bond force constants, bond orders, bond lengths and the electronegativities of bonded atoms has been demonstrated by Gordy as follows [20,21]

$$k = aN(\chi_A \chi_B / d^2)^{3/4} + b \quad (10)$$

where k is the bond force constant, d is the bond length, N is the bond order and, χ_A and χ_B are electronegativities of bonded atoms. a and b have different numerical values for different molecules/groups.

In 1993, T. Ghanty and S. K. Ghosh [22] demonstrated the interesting correlations between the hardness, polarizability and size of molecules. It has been proved that the softness of a molecule (σ) is proportional to bond length (r_e). Pearson who introduced chemical hardness and softness concepts has studied some diatomic hydride molecules (HX) and reached to the conclusion that there is a correlation between the dissociation energy and $k^{1/2}$ (k is force constant). In addition to this correlation, Pearson deduced a new equation regarding the calculation of force constants of diatomic covalent molecules. The equation is given

as follows [23].

$$kr_e = 77\chi_A^2 + 117. \quad (11)$$

In the equation, k is force constant, r_e is bond length, and χ_A is atomic electronegativity value which belongs to atom that is different from hydrogen in any diatomic hydride in Pauling units.

Towards the end of the twentieth century, K. Ohwada published some important theoretical studies relating to the calculation of bond force constants of diatomic molecules. In one of these, Ohwada derived a new formula under several reasonable assumptions to calculate the heteronuclear diatomic force constants (K_{AB}) based on homonuclear diatomic force constants (K_{AA} and K_{BB}) as [24]:

$$K_{AB} = (K_{AA} \cdot K_{BB})^{1/2} \quad (12)$$

Following this work, he improved the Eq. (12) through the second-order perturbation theory and presented the equation given below for the calculation of bond force constants of heteronuclear diatomic molecules [25].

$$K_{AB} = \xi^3 (K_{AA} \cdot K_{BB})^{1/2} \quad (13)$$

where ξ is correction factor and it is defined as $\xi = (R_{AA} \cdot R_{BB})^{1/2} / R_{AB}$ based on R_{AA} , R_{BB} and R_{AB} , the internuclear distances of diatomic molecules AA, BB and AB, respectively.

Despite the vast prospective of quantum chemical methods, there is still a need to understand the properties and behavior of molecules on the basis of simple empirical models that require no sophisticated calculations. The present work provides a simple empirical model for calculation of bond stretching frequencies of diatomic molecules. The present work is focused on investigating whether molecular hardness is useful to predict the force constants of some diatomic molecule groups. The goal is to present a new equation based on the relation between molecular hardness and bond length with force constant.

2. Theoretical model

From the above discussions it seems that the bond-stretching force constant k has some connection with the density functional theoretical parameters. Now let us ponder over the concepts of the bond stretching force constants, hardness and bond distance of diatomic molecules. It is unequivocal that the bond stretching force constant is intimately connected to the hardness and bond distance of the diatomic molecules. By definition, the chemical hardness is a measure of the resistance power of the chemical species towards electron cloud polarization or deformation. In 1997, S. Arulmozhiraja and P. Koldaivel [26] pointed out that "With increasing chemical hardness in diatomic molecules, either the force constants or binding energies of molecules increase" and "The chemical hardness is a better pointer of stability of the molecules that is the chemical potential". Thus it is expected that the bond stretching force constants is proportional to the hardness of diatomic molecules. Considering the definitions of bond stretching force constants and hardness of diatomic molecules, we can safely assume that $k \propto \eta_M$ when r_e and other parameters related to the bond stretching are constant. It is well known that k decreases with bond distance. Thus we can safely assume that $k \propto (1/r_e^2)$ when r_e and other parameters related to the bond stretching are constant. It is well known that k varies with all the quantities like electronegativity, hardness, bond order, bond distances etc. Now, Ghosh and Islam [27–30] based on the fundamental identity of the basic concept and the origin of the electronegativity and the hardness posited the conceptual commonality between the electronegativity and the hardness. There are several reports where k of diatomic molecules are expressed as a function of electronegativity we here consider the hardness of the molecule to compute the k .

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