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Study of Molecular and Electronic Properties of Some Diatomic Molecules

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Abstract

The theoretical calculations for ionization energies, electron affinities, electronegativities, hardnesses, softness, electrophilic index, HOMO and LUMO energies, and energy gap for alkali halides molecules (LiBr, NaBr and KBr) were done with the commonly used B3LYP and by using (DFT) level of theory using the basis set 6-311G(d, p). The results are in good agreement with the experimental measurements. Binding energies for these molecules were performed by using equation depending on dissociation energies, ionization energies, and electron affinities. The geometrics properties of these molecules in their ground state are determined by (DFT) method. Some of the parameters and potential energies are determined by applying for the theoretical program. The results show that the potential energy curve matches well with the fitting curve.

1. Introduction

The information of diatomic molecules and alkali halides such as LiBr, NaBr and KBr are useful and has been applied and used in a wide range of processes and materials, specially, in many industrial applications [1,2]. The spectroscopic parameters for LiBr, NaBr and KBr molecules in its ground state and some previous literatures for these molecules are until now limited [3-8]. In order to know the effect of the basis set on the spectroscopic parameters and potential energy curves, theoretical calculations were done by density functional theory (DFT) methods [9,10]. These calculations use the electron density $\rho(r)$ instead of Ψ (wave function); that due to the Hohenberg-Kohn theorems [11]. The molecular or atomic characteristics appear as a function of the electron density from a minimization of the molecular or atomic energy. According to Hohenberg and Kohn theorems, the number of electrons (N) with molecular or atomic energy (E) can be obtained using integration of $\rho(r)$ [9, 10].

$$\delta(E - \mu \int \rho(r)dr) = 0 \qquad (1)$$

The Euler equation is obtained

$$\mu = v(r) + \int \frac{\rho(r')}{|r - r'|}dr' + \frac{\delta T}{\delta \rho} + v_{XC}(r), \qquad (2)$$

μ : the chemical energy, T: the kinetic energy functional, $v(r)$:the external energy and$v_{XC}(r)$:the exchange-correlation energy, r and r' are the bond length and bond length at equilibrium respectively, therefore

$$v_{XC}(r) = \frac{\delta E_{XC}}{\delta \rho}\,. \qquad (3)$$

Where E_{XC}: derivative of $v_{XC}(r)$.
Kohn and Sham[12] changed equation (3) into a good determination tool by depending on orbitals in the kinetic energy. The scientific concepts of the Kohn and Shamorbitals were very important for scientists [13] showed for an atom:

$$\mu = \left\{ \begin{array}{ll} -IP & (Z-1<N<Z) \\ -EA & (Z<N<Z+1) \end{array} \right\}. \qquad (4)$$

Where Z: nuclear charge, IP: ionization potential, EA: electron affinity, and the chemical potential$\mu = \partial E/\partial N$.

The HOMO (Highest Occupied Molecular Orbital) and LUMO (lowest Unoccupied Molecular Orbital) energies have been used to estimate (IP) and (EA) respectively by Koopmans' theorem [14]. The average value of the HOMO and LUMO energies gives the electronegativity (χ) defined by Mulliken [15]. Also, the HOMO-LUMO gap is used to determine the hardness (η), and tow electronic properties can yield from this study (softness (s) and electrophilic (W))[16].

In alkali halides molecules, binding energies are usually represented in (I) charge-charge interaction, (II) charge-dipole interaction, dipole-dipole interaction, (III) a Van der Waals attraction, (IV) kinetic energy terms as the difference in rotational energy, vibrational energy and translational energy[17].

2. Computational methods

All theoretical calculations for Geometries electronic properties of the molecules in this work were optimized by applying DFT with B3LYP/6-311G(d, p) level and performed using the GAUSSIAN94 program[18].The HOMO and LUMO energies were estimated with the B3LYP/ aug-cc-pVTZ+1 basis set. The ionization potential (IP), electron affinities (EA) were estimated by equations [14]

$$-\varepsilon_{HOMO} \approx IP$$

$$-\varepsilon_{LUMO} \approx EA \qquad (5)$$

The hardness(η) and electronegativity (χ) calculations are by using finite difference approximation [14],

$$\chi = (\mathrm{IP} + \mathrm{EA})/2 \qquad (6)$$

$$\eta = (\mathrm{IP} - \mathrm{EA})/2 \qquad (7)$$

The softness (s) and electrophilic (W) are given by the equations [19,20]

$$s = 1/2\eta \qquad (8)$$

$$W = \chi^2/2\eta \qquad (9)$$

Also, in our calculations that binding energies B.E (i.e. the ionic dissociation energy) for diatomic molecules LiBr, NaBr and KBr are given by the relation [21]

$$B.E = D_e + IP - EA \qquad (10)$$

Where $D_e$is dissociation energy.

On the other hand, in this paper, the ground state geometries of LiBr, NaBr and KBr were fully optimized with the Density functional theory using the B3LYP method. The optimization and single point energy were evaluated at B3LYP/6-311++G(df, pd), B3LYP/6-311++G(2df , 2pd) and B3LYP/6-311++G(3df , 3pd) levels respectively. Dissociation energies D_e were calculated from the optimization. All (R_e, B_e, ω_e and $\omega_e\chi_e$), the equilibrium internuclear distance, rotational constant, harmonic vibrational wavenumber, and anharmonicity constant respectively were obtained with the dissociation energy and the single point energy scan results as the input file of Level 8.0 program[22]. The potential energy curve of LiBr, NaBr, and KBr in the ground state with the Level 8.0 fitting curves are evaluated and plotted using the B3LYP at many basis sets [22, 23].

Results and Discussion

In the beginning, the work of B3LYP and (DFT) level of theory using set 6-311G(d, p) in the investigation of molecular and electronic properties. The B3LYP functional has been selected with a high efficient to calculate all properties (equation (5) – equation (9)), as well as the energy gap for selection molecules. The tables 1 and 2 display these results.

The results of ionization potential show that LiBr, NaBr, and KBr molecules have a tendency to capture electrons or donating them. Ionization potential for LiBr molecule is greater than that for two remaining molecules, this leads to high energy for this molecule to be parallel with others and (IP) was gradually increasing with decrease the HOMO energy. Ionization potential for LiBr molecule is the largest (6.1200 eV). The electron affinity is a measure of the strength of an acceptor molecule in which it has a high EA and (EA) was slightly increasing with decrease (LUMO) energy, the electron affinity for NaBr is the largest (1.401 eV). Figure (1) shows the values and behavior of (IP and EA) comparing with molecules, and Figure (2) shows the relationship between HOMO-LUMO Energy Gaps with our studied molecules.

The result of energy gaps of KBr molecule is (3.160 eV) and less than that of the LiBr and NaBr molecules, therefore, decreasing the magnitude of energy gap enhances the conductivities of this molecule and also improves the solubility. With decreasing energy gap, easily the electrons can be excited from the ground state [5]. The calculated energy gaps of all molecules are closer to the previous experimental magnitudes [5].

Table 1: (-E_{HOMO}), (-E_{LUMO}), HOMO-LUMO Energy Gap for LiBr, NaBr and KBr molecules

Molecules	**(-E_{HOMO}) (eV)**	**(-E_{LUMO}) (eV)**	**E_{gap}(eV)**
LiBr	6.120 6.542[5]	0.911 1.731[5]	5.209 4.811[5]
NaBr	5.132 6.034[5]	1.401 2.122[5]	3.731 3.912[5]
KBr	4.261 5.476[5]	1.101 1.806[5]	3.160 3.670[5]

Table 2: Calculated (IP), (EA), (χ), (η), (S), (ω) for LiBr, NaBr and KBr molecules.

Molecules	**IP(eV)**	**EA(eV)**	**χ (e V)**	**η(e V)**	**S(eV)**	**ω (eV)**
LiBr	6.1200 9.310[8]	0.9110 0.660[8]	3.5155 4.990[8]	2.6045 8.650[8]	0.1919 ----	2.3726 ----
NaBr	5.132 8.300[8]	1.401 0.790[8]	3.2665 4.550[8]	1.8655 7.5100[8]	0.2680 ----	2.8599 ----
KBr	4.261 7.8900[8]	1.101 0.6400[8]	2.681 4.270[8]	1.58 7.2500[8]	0.3164 ----	2.2746 ----

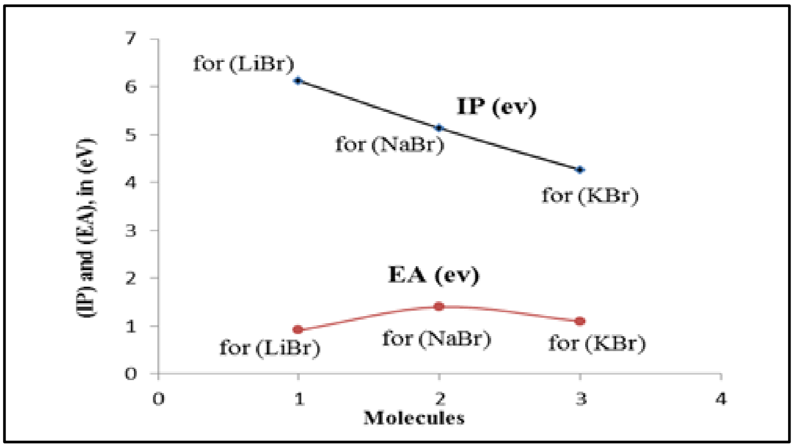

Figure 1. Ionization potential (IP) and Electron affinity (EA) for studied molecules in (eV)

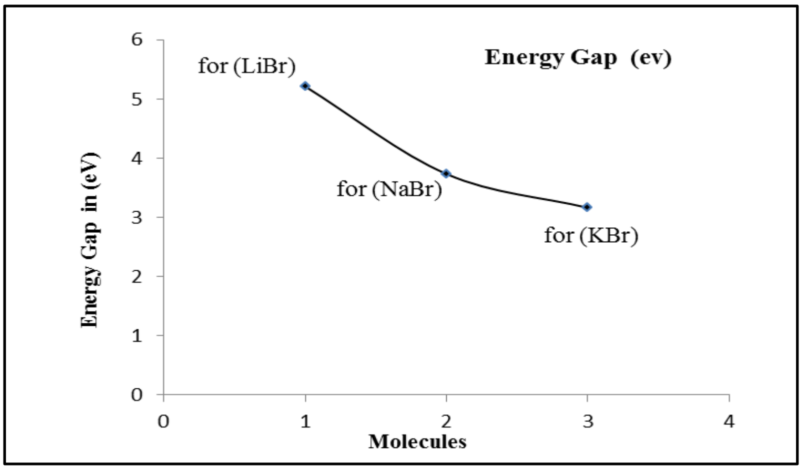

Figure 2. HOMO-LUMO Energy gap for studied molecules in (eV)

Figure (3) shows the relation between the (χ), (η), (S), (ω) and studied molecules, it is obvious from this figure that LiBr molecule has an electronegativity greater than (a chemical potential less than) that for other molecules, that means the electrons in LiBr molecule have a large escaping tendency. The behavior of hardness and electronegativity for LiBr molecule shows magnitudes larger than these for NaBr and KBr molecules, and fewer magnitudes of KBr molecule (1.58 eV) comparing with NaBr and LiBr molecules, therefore that give

KBrmolecule more softness. The behavior of Electrophilic index of NaBr molecule shows large magnitudes for this molecule than these for KBr and LiBr molecules. The behavior of softness of KBr molecule shows magnitudes larger than these for NaBr and LiBr molecules, it is clear that the increasing of softness is the main future as a sign for that band gap goes to be rather soft. This behavior gives this molecule more electrophilicity than other molecules, NaBr molecule has (ω = 2.8599 eV), while LiBr has (ω = 2.3726 eV) and KBr has (ω = 2.2746 eV). These results of all molecules are closer to the experimental values [8].

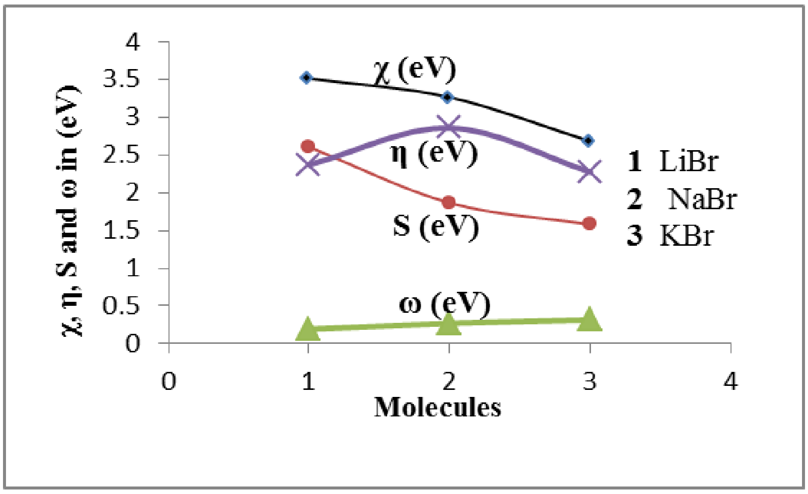

Figure 3. Electronegativity (χ), Hardness (η), softness(S), electrophilic index(ω) for studied molecules in (eV)

The geometric optimization and single point energy calculation of LiBr, NaBr and KBr molecules in the ground states were carried out at B3LYP/6-311++G(df, pd), B3LYP/6-311++G(2df, 2pd), and B3LYP/6-311++G(3df, 3pd) levels respectively.

The B3LYP calculation results are used as the input for the Level 8.0 to solve the nuclear Schrödinger equation and to calculate the spectroscopic constants. The calculated spectroscopic constants (including R_e, D_e, B_e, $\omega_e$and $\omega_e\chi_e$), of all molecules in the ground states, the existing experimental results [3,4, 17, 24]with our calculationsare summarized in (Tables 3 - 5). These tables show that the equilibrium bond distances (R_e) decrease from 6-311++G(df, pd) to 6-311++G(3df, 3pd) for all molecules, which are in agreement with the experimental values.

Also, the Potential energy curves and spectroscopic constants of these molecules calculated using the same basis sets and the Level 8.0 fitting curves are plotted in (Figures 4 – 6). These figures show that the Level 8.0 fitting curves agree well with the computed potential energy curves.

The dissociation energies (D_e) values increase from 6-311++G(df , pd) to 6-311++G(3df , 3pd) and these values are closer to the experimental values. The harmonic vibrational wavenumbers (ω_e) also increase with the improvement of the quality of these basis sets, although the values are lower than the experimental values [3, 4] by about 46 cm^{-1} for LiBr molecule, 45 cm^{-1} for NaBr molecule and 44 cm^{-1} for KBr molecule. However, these results are closer to another theoretical value [4]. It is obvious from our tables, our anharmonicity constant ($\omega_e\chi_e$) and the rotational constants (B_e) values agree well with the experimental values, our values increase with the quality of basis sets; these values agree very well with the experimental value[3, 4].

Table 3. Spectroscopic constants of LiBr in the ground state calculated with Level 8.0

Spectroscopic constants	**Basis sets**			**Experimental values**
	6-311++G (df ,pd)	6-311++G (2df ,2pd)	6-311++G (3df ,3pd)	
D_e (ev)	1.2245	1.3662	1.3825	2.159 [24]
$\omega_e(cm^{-1})$	530.1	531.2	532.4	576 [3, 4]
$\omega_e\chi_e(cm^{-1})$	4.43	4.37	4.49	4.28[3, 4]
R_e,Å	2.235	2.179	2.110	2.170 [17]
B_e, cm^{-1}	0.5755	0.5776	0.5790	0.5553 [24]

Table 4. Spectroscopic constants of NaBr in the ground state calculated with Level 8.0

Spectroscopic constants	**Basis sets**			**Experimental values**
	6-311++G(df ,pd)	6-311++G(2df ,2pd)	6-311++G(3df ,3pd)	
D_e (eV)	1.9795	2.0136	2.0357	1.553 [24]
ω_e(cm^{-1})	299.1	300.1	301.2	302 [3, 4]
$\omega_e\chi_e$(cm^{-1})	1.40	1.31	1.42	1.50 [3, 4]
R_e,Å	2.588	2.586	2.573	2.502 [17]
B_e, cm^{-1}	0.1633	0.1674	0.1688	0.1512 [24]

Table 5. Spectroscopic constants of KBr in the ground state calculated with Level 8.0

Spectroscopic constants	**Basis sets**			**Experimental values**
	6-311++G (df ,pd)	6-311++G (2df ,2pd)	6-311++G (3df ,3pd)	
D_e (eV)	1.4316	1.5262	1.5733	2.167 [24]
ω_e(cm^{-1})	205	206.6	207.2	213 [3, 4]
$\omega_e\chi_e$(cm^{-1})	0.900	0.910	0.972	0.80 [3, 4]
R_e,Å	2.899	2.896	2.891	2.821 [17]
B_e, cm^{-1}	0.0733	0.1002	0.112	0.0812 [24]

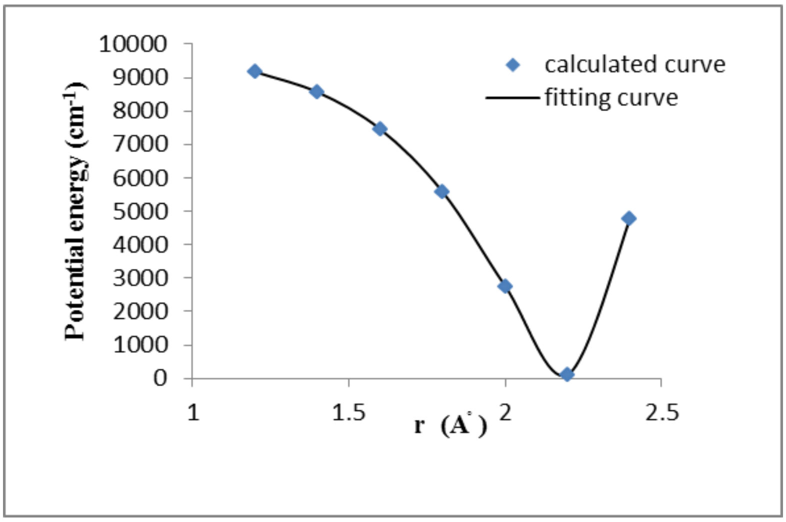

Figure 4. Potential energy curves of LiBr molecule in the ground state.

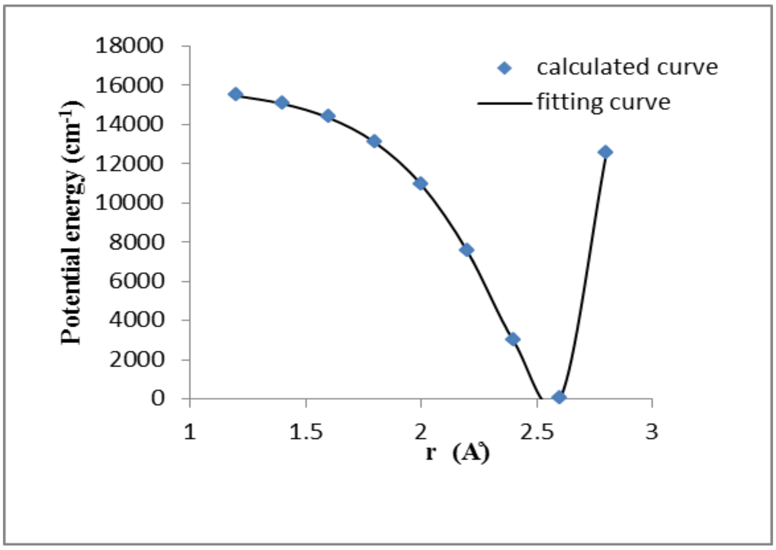

Figure 5. Potential energy curves of NaBr molecule in the ground state.

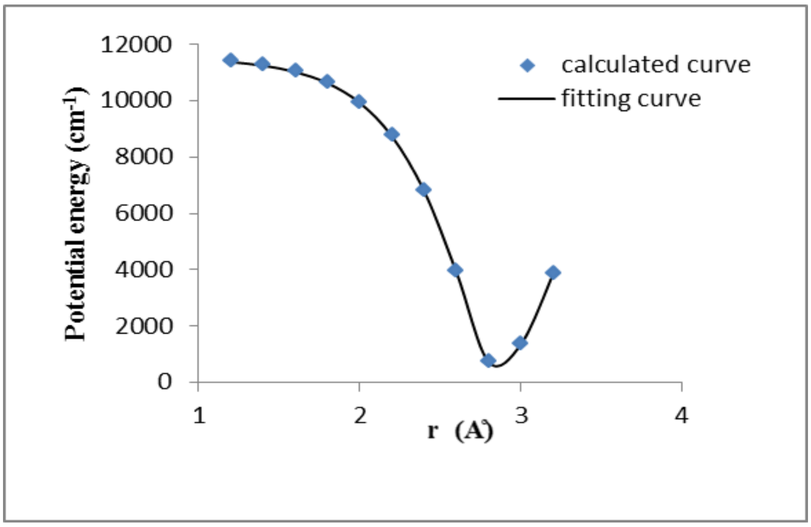

Figure 6. Potential energy curves of KBr molecule in the ground state.

Results of binding energy, (table 6), appeared high value (148.630 Kcal/mol) for LiBr molecule and low binding energy (131.604 Kcal/mol for NaBr and 104.845 Kcal/mol for KBr). These results indicate to the convergence with previous studies [25].

Table 6. Values of binding energies (B.E) for LiBr, NaBr and KBr molecules

Molecules	B.E kcal/mol	B.E kcal/mol [25]
LiBr	148.630	142.700
NaBr	131.604	124.400
KBr	104.845	109.100

Conclusions

A theoretical investigation by the (DFT) B3LYP level with the basis set 6-311G(d, p) leads to knowledge that ionization potential appear the studied molecules have a tendency to capture electrons. High binding energy and high energy gap for LiBr molecule due to IP is greater than that for other molecules. Also, the calculations by the (DFT) B3LYP method are very useful to know the Potential energy curves and spectroscopic constants of these molecules. The Level 8.0 fitting curve is important method of comparing curves, our results (R_e, D_e, B_e, ω_e, $\omega_e\chi_e$ and B.E), converge so well with the experimental values, so it is very useful for future reference.

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