Theoretical Spectroscopic Study for Some Diatomic Molecules

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Abstract

In this work, four electronic states ($X^1\Sigma^+$, $A^3\Pi_0$, $B^3\Pi_1$, and $C^1\Pi_0$) of some diatomic molecules (InF and InCl) was studied by TD-DFT with energy represented by the exchange-correlation energy. The SAOP/ATZP model was applied here to determine all parameters (r_e, B_e, D_e, ω_e, $\omega_e\chi_e$, T_e, α_e, and E_n° were determined to creation reliable values for electron spectroscopy. Also, another set of this calculation has been used represented by two theoretical models: ATZP and et-QZ3P-xD model. Therefore these theoretical models for ($X^1\Sigma^+$) and ($A^3\Pi_0$, $B^3\Pi_1$, and $C^1\Pi_0$) of the molecules have been compared with many values, theoretical and experimental values, and appear convergence in values with simple error %. Our results showed that the TD-DFT with basis set in the present work is important for the estimation of spectroscopic parameters and constants for our molecules and the ATZP model is very close to et-QZ3P-xD model in all electronic states for InF and InCl molecules except some of the constants such as (B_e).

Keywords: spectroscopic parameters, diatomic molecules, DFT.

Introduction

Indium halides are an important system to work with spectroscopic investigations and scientific lines in chemical, physical and astrophysical fields. For the last years, most researchers studies were about metal halides, that due to their potential applications. These are used in the lighting industry, for example diatomic indium halides have been subject to theoretical and experimental calculations [1]. The electronic spectrum of (InF and InCl) molecules appears in three band systems ($A^3\,\Pi_0$-$X^1\,\Sigma^+$, $B^3\,\Pi_1$-$X^1\,\Sigma^+$, and $C^1\,\Pi_0$-$X^1\,\Sigma^+$) transitions and observed as first studied by researchers in 1952 [2].

At recent years, the physical and chemical properties of indium halides have great interest because of their application in the development of some semiconductor devices. In 1955, R.F. Barrow et al.[3] studied the rotational analyses of several bands of the A–X and B–X systems of InF molecule, In 1969, F.J. Lovas et al. [4] made high-temperature mass spectrometric studies of InF molecule of the dissociation energy.

Recently spectroscopy offers direct determinations of parameters from the potential energy curves in which a molecule resides [5]. To know the properties of molecular spectroscopy we depend upon the molecular states for all electronic states. The ground state is more determined than the excited state, often with incomplete information available [6]. With a high exactitude, the spectroscopic parameters can be estimated, by curves fitting [5]. Spectroscopic parameters are very important to determine the spectrum, which is employed as a way to give new spectroscopic theoretical investigations, as the basis set influence, the electron correlation influence [7]. The spectroscopic parameters of all molecules are necessary for poorly characterized electronic states or yet experimentally unknown [8].

The Density Functional Theory (DFT)[9] has been used for calculating some of the spectroscopic electronic state parameters. Accordingly, DFT methods are used in many chemical applications [8]. Therefore, the advancement of DFT can be used for exactitude potentials, also, give the exactitude estimation of highest electronic states [8].

Some of the previous studies of the (TD-DFT) [10] have been used to calculate transition probability and excitation energy. Choosing TD-DFT methods is accessible in more theoretical packages, and in quantum chemical calculations, one needs a bigger number of the Gaussian-type basis than a Slater-type basis [11]. STO set has been improved and enter into theoretical calculations. Chong [7] evolved a method called by DZP (ADZP) method and TZP (ATZP) method in his calculations.

In our study, another model (et-QZ3P-xD) [12] is compared with the improved ATZP set. The determination of spectroscopic parameters of the four states of InF and InCl molecules requires knowing the location of potential curves carefully.

Method of computations

In our study, we use the TD-DFT method for calculation, the electronic states ($X^1\Sigma^+$, $A^3\Pi_0$, $B^3\Pi_1$, and $C^1\Pi_0$) of our molecules (InF and InCl) can be studied by this method. The SAOP/ATZP model was used in this work to calculate all spectroscopic parameters and constants: Excitation energy (T_e), bond length at equilibrium (r_e), the rotational constant (B_e), harmonic vibrational frequency (ω_e), vibrational anharmonicity ($\omega_e\chi_e$), zero-point energy (E_n°), centrifugal distortion constant (D_e), the vibration–rotation constant (α_e). Also, another set of this calculation has been used represented by TD–DFT (SAOP)/et-QZ3P-xD model. which was used to model for ($X^1\Sigma^+$) and ($A^3\Pi_0$, $B^3\Pi_1$, and $C^1\Pi_0$) states of InF and InCl molecules. In this model, the advanced ATZP set [7] was applied. Three points determine the creation of our required parameters: (I) generation of the potential energy surfaces by two theoretical models ((SAOP)/et-QZ3P-xD and SAOP)/ATZP); (II) potential fitting of the electronic states, and (III) parameters calculation. The spectroscopic parameters and constants of all the electronic states are determined by fitted analytical potential curves.

By dependending on the Quantum approximation and the results of rovibrational energy levels, any potential energy $U_n(\rho)$ for the electronic states can be written as [13]:

$$U_n(\rho) = \sum_{i=1}^{6} c_i\, \rho^i \qquad (1)$$

Where c_i is spectral constant at (i=1,…,6), and ρ^i is a spectral parameter equals to ($r-r_e$); n= 0,…, 7; (i.e. ground = 0). For all ground and excited state determined, the calculations were done using two theoretical models. All calculations were done applying the ADF theoretical program [14,15], and TD-DFT. The potential energy curve was fitted to equation (1) for all electronic states. Then, in this work, two basis sets were examined, they are labeled as efficient and large basis sets; the established et-QZ3P-xD is the large basis set, where x = 1 or 2 according to atoms. The (ATZP) is the efficient basis set with x = 1or 0 [7].. The potential energy can be written as follows [16]:

$$G_V \simeq \omega_e\left(V+\frac{1}{2}\right) - \omega_e\chi_e\left(V+\frac{1}{2}\right)^2 \qquad (2)$$

where (ω_e) is harmonic frequency, ($\omega_e\chi_e$) is anharmonic frequency and (v) is vibration quantum number . Also, vibrational zero-point energy (ZPE) can be written as[16]:

$$E_n(V=0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e\chi_e \qquad (3)$$

$$F_V(J) = \frac{E_V(J)}{hc} = B_V J(J+1) - D_V J^2(J+1)^2 + \cdots \qquad (4)$$

Where, $F_V(J)$: the vibrational term, (J): the angular momentum and (B_V): the rotational constant at (v- state) [16]:

$$B_V = B_e - \alpha_e\left(V+\frac{1}{2}\right) + \cdots \qquad (5)$$

Where B_e: rotational constant at equilibrium and α_e: vibrational– rotational constant.

The total energy E_{nvJ} can be written as[13]

$$E_{nVJ} = T_e(n) + G(V) + F(J) \qquad (6)$$

Where $T_e(n)$ is the transitional energy, the spectroscopic constants were determined in a program called VIBROT [17].

Results and discussion

The Spectroscopic investigation for all constants (r_e, ω_e, α_e, $\omega_e\chi_e$, T_e , D_e, B_e, and E_n°) have been estimated by two models (ATZP and et-QZ3PxD) for ($X^1\Sigma^+$, $A^3\Pi_0$, $B^3\Pi_1$, and $C^1\Pi_0$) states of InF and InCl molecules and presented in tables 1 and 2. Also, errors % in the states for InF and InCl have been determined, which depended on constants above. These errors are given in figures (1–7). These parameters were created by dependending on (ATZP) and (et-QZ3P-xD) sets and were expressed in figures (8 – 11).

The errors in r_e estimated by the TD- DFT(SAOP)/ATZP model and Figure 1 shows that. The errors are about of 0.45%, this is close to researcher's results [18] for InCl and [19] for InF. The constant B_e is associated to r_e as below[16]:

$$B_e = \frac{\hbar}{4\pi\mu r_e^2}$$

Where ħ is Dirac constant, μ is reduced mass and r_e is bond length at equilibrium, they are the prospect to have symmetric alterations as r_e but in a reciprocal position, this is because of the inverse relationship between B_e and r_e. The errors in B_e have been expressed in figure 2 for all states of InF and InCl.

However, in a ground state and excited state, the efficient basis set and the larger basis set gave bond lengths and rotational constants for InF and InCl molecules very convergent with the experimental values [18] for InCl and [19] for InF (see table 1 and 2).

Figures (3-a and 3-b) provide an appraisement of the exactitude of the harmonic vibrational frequency ω_e, which is the theoretical result, with the two models. Also, our theoretical value of (ω_e) in the ground state is proximate to researcher's results. The centrifugal distortion constant D_e (figure 4) exhibit fairly accurate agreement with experiment.

The theoretical estimation of $(\omega_e\chi_e)$ has its prominence in high exactitude estimations of experimental values. The vibrational– rotational constant (α_e) depend upon the third derivative of the potential energy curves, but the fourth derivative is used to obtain on $(\omega_e\chi_e)$. The errors are the outcome of the first and second excited states. The errors in constants in ground states are by et-QZ3P-xD model less than ATZP model for InF molecule, but in InCl molecule, the errors were in ATZP model less than the et-QZ3P-xD model. The errors in other excited states were convergent as shown in figures (5-a and 5-b).

The constant (α_e) is associated with other parameters via [16]

$$\propto_e = \frac{6\sqrt{\omega_e\chi_e B_e^3} - 6B_e^2}{\omega_e}$$

Figures (6-a and 6-b) show convergence in the performance of the effective set and performance of the larger set. For normal molecules, zero-point energy (ZPE) is small as shown in the tables. Also, producing the ZPE in this study as a "spectroscopic constant" is an important process. Figure 7 shows the errors of the estimation ZPE by these models, which also are convergent.

Adiabatic excitation energy, (T_e) of molecules has been discussed in this study for InF and InCl molecule as showen in tables (1 and 2) and figures (8-11), where values of (T_e) were zero for ground states and convergent values for excited states with experimental values.

Figure 8 shows a comparison between theoretical models in the ground states of InF molecule by depending on "absolute average percentage deviation (AAPD)" for the diatomic molecular parameters. From this figure, the SAOP give a good agreement with the experimental results in the ground states. The et-QZ3P-xD model shows error % less than the ATZP model for all constants. The high error % was clear in estimating the anharmonic $\omega_e\chi_e$ and the rotational constant (B_e) in this figure.

Also, figure 9 shows a comparison between theoretical models in the three lowest-lying excited states of InF molecule. From this figure, the TD-DFT(SAOP)/et-QZ3P-xD model appears error % less than the TD-DFT(SAOP)/ATZP model for all constants except rotational constant (B_e).

In Figure 10, the results show convergence in errors% between theoretical models of the constants for ground states of InCl molecule except for the constants $(\omega_e\chi_e)$ and (B_e) which show high errors in the TD-DFT(SAOP)/et-QZ3P-xD model comparing with the TD-DFT(SAOP)/ATZP model, That is, due to the inverse relationship between the two constants (B_e and r_e).

In figure 11, the results show convergence in errors% between theoretical models of the constants for three lowest-lying excited states of InCl molecule except for the constants $(\omega_e\chi_e)$ which show high errors in the ATZP model comparing with the et-QZ3P-xD model, therefore here et-QZ3P-xD model is better than ATZP model, and agree with experimental values.

In general, two theoretical models for $X^1\Sigma^+$state and next three low-lying electronic states ($A^3\Pi_0$, $B^3\Pi_1$, and $C^1\Pi_0$) of the molecules have been compared with theoretical and experimental values, and the results show convergence in values with simple error %. Our results have shown that the TD-DFT in conjunction with basis set in this study is an important for the estimation of spectroscopic parameters for ground and excited states of InF and InCl molecules,

Conclusion

The important conclusion from our results is the ATZP basis set which is very close to larger et-QZ3P-xD basis set, as shown in tables and figures in previous results section. That is in all electronic states of InF and InCl molecules except some of the constants such as (B_e) which have different behavior in sometimes.

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Table(1): Spectroscopic constants for the electronic states of InF molecule.

State	**Method**	**r_e (Å)**	**T_e (cm^{-1})**	**ω_e (cm^{-1})**	**$\omega_e\chi_e$ (cm^{-1})**	**$D_e\times10^8$ (cm^{-1})**	**α_e (cm^{-1})**	**B_e (cm^{-1})**	**E_n° (cm^{-1})**
$X^1\Sigma^+$	et-QZ3P-xD	1.972	0	534.112	2.5212	25.2400	185231	0.2470	266.42
	ATZP	1.976	0	544.144	2.5000	25.1600	185200	0.2410	271.44
	Expt.[19]	1.985	0	535.350	2.6180	25.2096	187855	0.2628	267.02
$A^3\Pi_0$	et-QZ3P-xD	1.932	29335	574.311	3.5800	25.1100	198011	0.2880	286.26
	ATZP	1.933	29156	573.000	3.5801	25.0000	198000	0.2720	285.60
	Expt.[19]	1.985	28145	575.200	3.6700	25.0000	200000	0.2732	286.68
$B^3\Pi_1$	et-QZ3P-xD	1.940	31221	588.000	2.9100	25.1112	201006	0.3050	293.19
	ATZP	1.945	31040	582.300	2.9000	25.1000	201004	0.2725	290.42
	Expt.[19]	1.944	31255	572.200	2.6300	25.0000	201000	0.2736	285.44
$C^1\Pi_0$	et-QZ3P-xD	1.952	41765	461.244	7.1311	36.5200	492000	0.2510	228.83
	ATZP	1.962	41534	460.622	7.2461	36.4100	491110	0.2441	228.49
	Expt.[19]	1.967	42809	463.900	7.3500	36.5000	500000	0.2670	230.11

Table (2): Spectroscopic constants for the electronic states of InCl molecule.

state	**method**	**r_e (Å)**	**T_e (cm^{-1})**	**ω_e (cm^{-1})**	**$\omega_e\chi_e$ (cm^{-1})**	**$D_e\times10^8$ (cm^{-1})**	**α_e (cm^{-1})**	**B_e (cm^{-1})**	**E_n° (cm^{-1})**
$X^1\Sigma^+$	et-QZ3P-xD	2.413	0	316.324	1.3241	5.1100	51821	0.1277	157.83
	ATZP	2.417	0	311.881	1.1022	5.0902	51744	0.1122	155.66
	Expt. [18]	2.402	0	317.389	1.0320	5.1612	51737	0.1089	158.43
$A^3\Pi_0$	et-QZ3P-xD	2.330	27821	338.112	1.9442	5.2911	67992	0.1269	168.56
	ATZP	2.334	27423	333.001	1.9331	5.3477	64515	0.1392	166.01
	Expt. [18]	2.333	27778	340.040	1.8800	5.2660	66780	0.1152	169.55
$B^3\Pi_1$	et-QZ3P-xD	2.332	28001	337.901	2.3022	5.9141	79821	0.2824	168.37
	ATZP	2.337	28433	335.551	2.2717	6.0012	76999	0.9065	167.20
	Expt. [18]	2.338	28563	339.100	2.1930	5.9000	78740	0.1149	169.00
$C^1\Pi_0$	et-QZ3P-xD	2.441	37423	176.010	12.8220	14.2076	36879	0.4822	84.79
	ATZP	2.462	37200	174.261	12.0016	15.0333	35662	0.5666	84.13
	Expt. [18]	2.458	37568	177.270	12.5890	14.9500	36654	0.1040	85.48

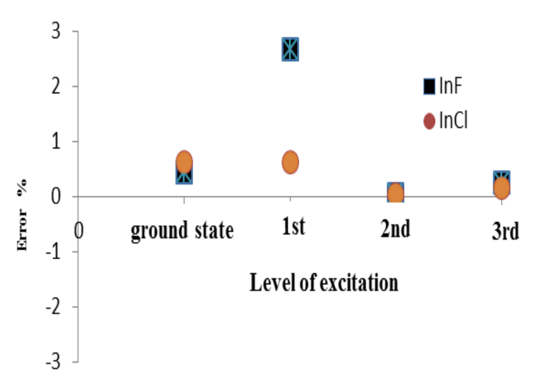

Figure (1). Error in (r_e) as result of the ATZP model

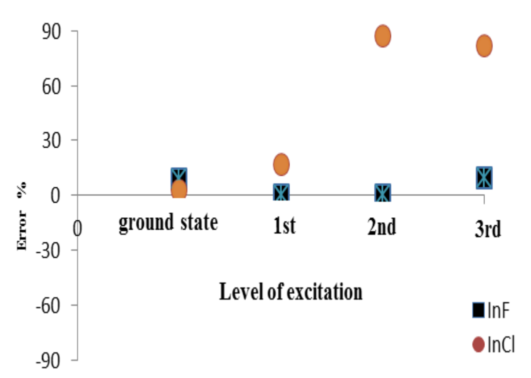

Figure (2). Error in (B_e) as result of the ATZP model

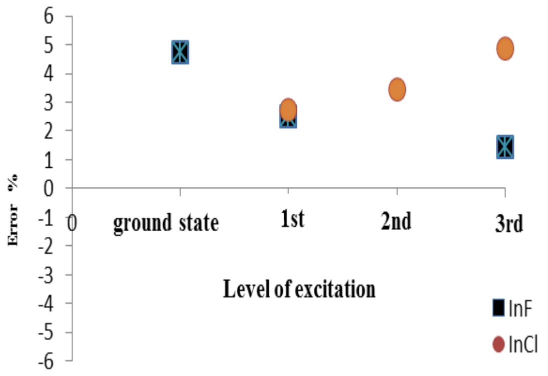

Figure (3-a). Error in (ω_e) as result of ATZP model

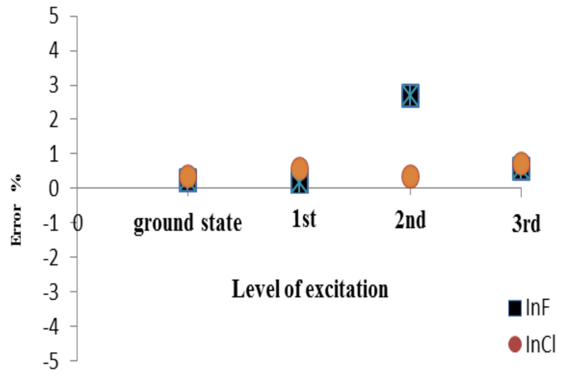

Figure (3-b). Error in (ω_e) as result of the et-QZ3P-xD model

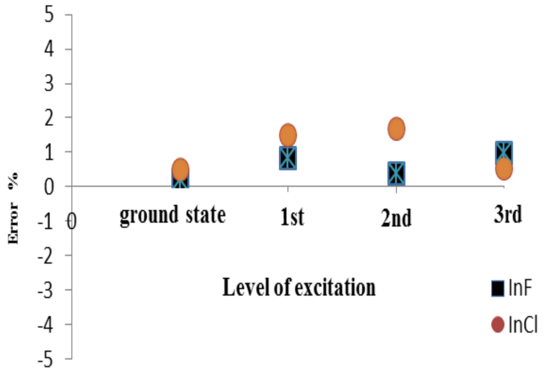

Figure (4). Error in (D_e) as result of the ATZP model

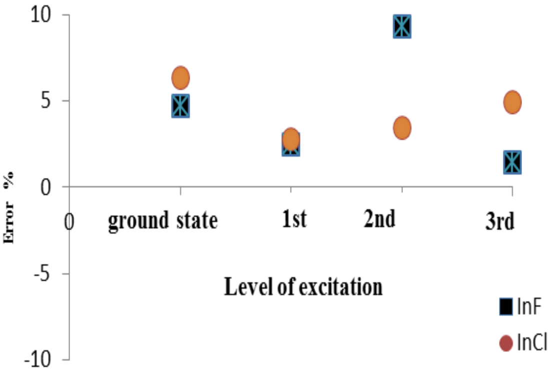

Figure (5-a). Error in ($\omega_e\chi_e$) as result of the ATZP model

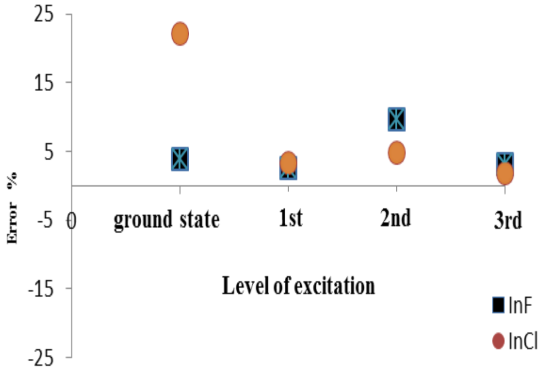

Figure (5-b). Error in ($\omega_e\chi_e$) as result of et-QZ3P-xD model

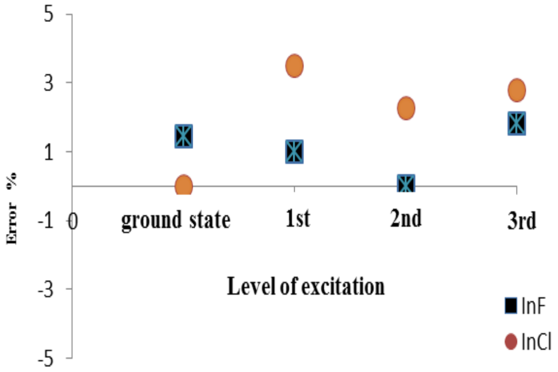

Figure (6-a). Error in (α_e) as result of the ATZP model

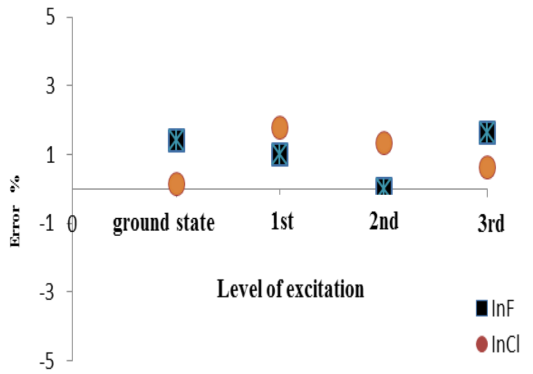

Figure (6-b). Error in (α_e) as aresult of the et-QZ3P-xD model

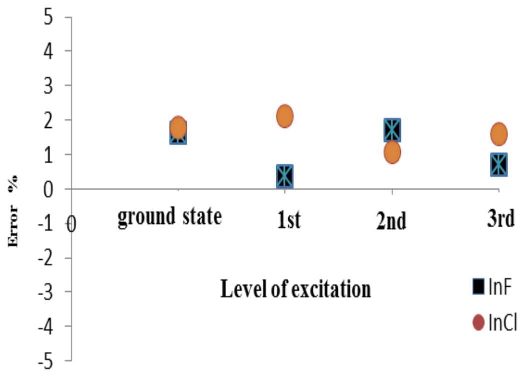

Figure (7). Error in (E_n°) as result of the ATZP model

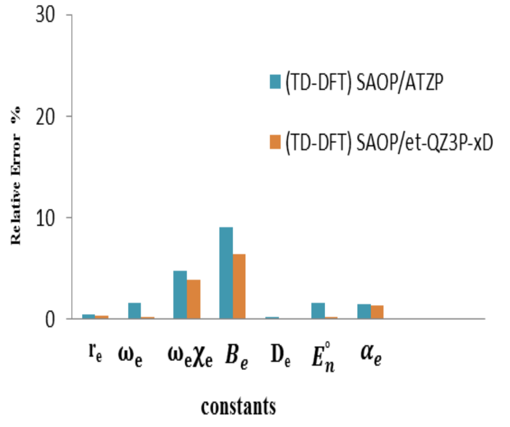

Figure (8). Comparision between theoretical models in the ground states of InF molecule.

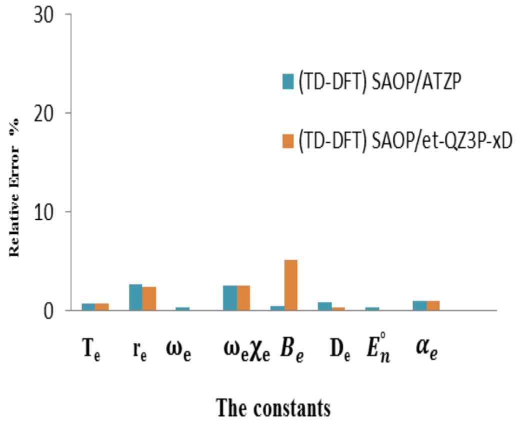

Figure (9). Comparision between theoretical models in the excited states of InF molecule .

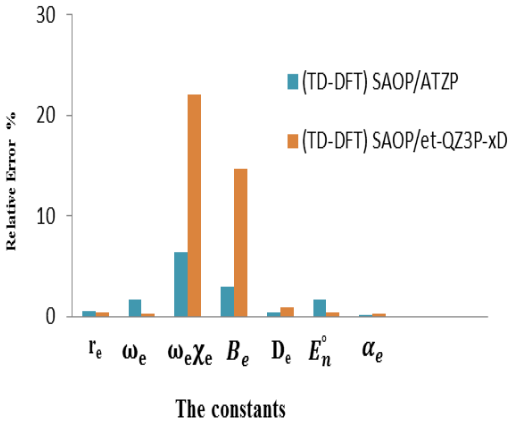

Figure (10). Comparision between theoretical models in the ground states of InCl molecule.

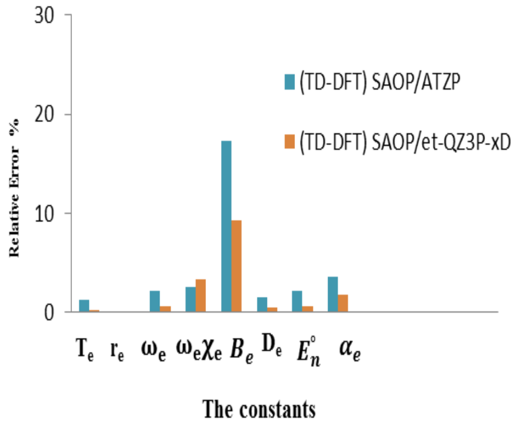

Figure (11). Comparision between theoretical models in the excited statesofInCl molecule .