

Electronic Structure Studies with Spin-Orbit Coupling Effect of the Molecule TII

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Abstract: - To study the low-lying electronic states of the TII molecule, the electronic structure of this molecule has been investigated via an ab initio Complete Active Space Self Consistent Field and the Multireference Configuration Interaction with Davidson correction calculation (CASSCF/MRCI+Q). In the representations of $^{2s+1}\Lambda^{(+/ -)}$ and $\Omega^{(\pm)}$, the adiabatic potential energy curves (PECs) along with static and transition dipole moment (DM) curves for 19 low-lying electronic states for TII molecule have been investigated. For the low-lying electronic states of this molecule, the spectroscopic constants R_e , T_e , ω_e , and B_e , are provided. Based on the data obtained, this molecule is not a candidate for a Doppler laser cooling study.

Key-Words: - ab initio calculation, electronic structure, spin-orbit coupling, potential energy curves, dipole moment, spectroscopic constants, diatomic molecule.

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1 Introduction

With a spin-orbit splitting of 7793 cm^{-1} , thallium exhibits strong relativistic effects as a heavy metal belonging to the GIII-A group, which are anticipated to be significant for chemical bonding, [1]. It is well known that thallium compounds make valuable materials, such as high-temperature superconducting materials and catalysts for organic synthesis, [2], [3]. Thallium halides have drawn much attention from researchers because they are among the earliest thallium compounds to be produced. The spectra and dynamics of the electronic states of these compounds have been the subject of several experimental and theoretical studies.

Here, we use gaseous thallium mono-halide as straightforward representations of thallium compounds. Both theorists and experimentalists have long been drawn to these systems. For TIX (X = F, Cl, Br, and I), several spectroscopic measurements have been made up to this point, [4]. However, most excited states' geometrical and spectroscopic characteristics are yet unknown. The ground state and some excited electronic states of TII were investigated, [4]. Spin-orbit coupling (SOC) significantly impacts spectroscopy and dynamics. The SOC effect can cause pre-dissociations between Λ -S states with various spin

multiplicities and multiple avoided crossings of $\Omega^{(\pm)}$ states, [5].

The present work on the molecule TII is a part of our research project on iodine compounds such as CaI [6], BaI [7], MgI [8] and BeI [9]. Since there is some available data for electronic states in the literature on the molecule TII, we expect to supply pleasant details for theoretical studies of this molecule, [4]. Our powerful motive is to profoundly analyze the molecule's ground with excited states with their complete spectroscopic and spin-orbit studies in the current work.

Because of this absence, an ab initio method with a Complete Active Space Self Consistent Field has been used with Davidson correction (CASSCF/MRCI+Q) to calculate the potential energy (PECs), the static and transition dipole moment curves (DMCs), the Franck-Condon factor FCF, and the radiative lifetime. In the representations, $^{2s+1}\Lambda^{(+/ -)}$ and $\Omega^{(\pm)}$, 19 low-lying electronic states have been investigated for the molecule of TII where most of the investigated data are presented here for the first time.

2 Computational Methods

The state average Complete Active Self Consistent Field (CASSCF)/Multireference Configuration

Interaction (MRCI + Q) has been used to investigate the singlet and triplet electronic states of the TII molecule. With the graphical interface GABEDIT, [10]. The computational chemistry program MOLPRO (a software package developed for accurate ab initio quantum chemistry calculations) is used to accomplish these calculations, [11].

The Born-Oppenheimer approximation was used to obtain the potential energy curves. Using the customized core polarization potentials (CPP) and energy-consistent effective core potentials (ECP) from the Stuttgart/Cologne Group, the relativistic effects and core electrons were treated. The MRCI and CASSCF methods, along with selected basis sets, were used to describe the valence electrons.

For the TII molecule, the ECP60MDF basis set is used for the TI atom with 21 valence electrons distributed as $5s^2 5p^6 5d^{10} 6s^2 6p^1$, [12]. For the I atom, the basis set ECP46MDF is considered with seven valence electrons distributed as $5s^2 5p^5$, [13]. For the considered molecule TII, 9 occupied shells are investigated in symmetry 1, 4 in symmetries (2 and 3), and only 1 shell in symmetry 4. For the closed shells, five are considered in symmetry 1, 2 in symmetries (2 and 3), and 1 shell in symmetry 4. We chose ECP as a basis for TI and I atoms by referring to many papers on these atoms published in the literature, [14], [15], [16].

The diatomic molecules belong to $C_{\infty v}$, and because of the limitation of the MOLPRO, it turns to its subgroup C_{2v} , which has four irreducible representations (a1, b1, b2, a2). The active space for the TII molecule is 4σ (TI: $6p_0, 7s; I: 5p_0, 6s$), 2π (TI: $6p_{\pm 1}; I: 5p_{\pm 1}$;) and 0δ , with the irreducible representation $7a_1, 3b_1, 3b_2$, and $1a_2$ noted by [4, 2, 2, 0]. To obtain the potential energy curves, the estimated energy points are connected using the avoided-crossing rule for electronic states that belong to the same irreducible representation of the single/double point group $C_{\infty v}$. The one-dimensional Born-Oppenheimer Schrödinger equation is used to obtain the spectroscopic constants including R_e (equilibrium bond length), T_e (transition energy), ω_e (harmonic constant), and B_e (rotational constant).

3 Results and Discussion

3.1 Spectroscopic Constants

With and without spin-orbit coupling, the singlet and triplet electronic states of the molecule TII are investigated. The spectroscopic constants (Transition energies, internuclear distances, harmonic vibrational frequencies) for the bound

states can be computed using the X-Poly or X-min programs. The PECs are first fitted to a polynomial function ($U(r) = a_0 + a_1r + a_2r^2 + \dots$) to reproduce the ab initio values. After that, the constants are computed analytically by their definitions.

The operating system that is being used determines which program is selected. The Windows operating system is used with X-poly, and the Ubuntu operating system is used with X-min. However, both provide the same reliability and accuracy. Table 1 and Table 2 present the PECs spectroscopic constants that we computed using the X-poly program for the different electronic states.

Table 1. Spectroscopic constants T_e , R_e , ω_e , and B_e of the molecule TII (with spin-orbit coupling)

states	T_e (cm ⁻¹)	ω_e (cm ⁻¹)	R_e (Å)	B_e (cm ⁻¹)
(1) ¹ Σ^+_{0g}	0.00	141.64	5.4712	0.0257
(1) ¹ Π_{0g}	19506.20	20.37	4.2567	0.0119
(1) ¹ Δ_1	24169.04	29.70	4.0363	0.0132
(1) ¹ Σ^+_{0u}	24463.03	20.86	4.2342	0.0120
(1) ¹ Π_1	24696.92	19.78	5.4815	0.0071
(1) ¹ Σ^+_1	24758.26	15.71	5.9989	0.0601
(1) ¹ Δ_2	24942.12	49.20	4.8681	0.0091
(2) ¹ Δ_1	29702.54	23.34	4.2024	0.0122

Table 2. Spectroscopic constants T_e , R_e , ω_e and B_e of the molecule TII (without spin-orbit coupling)

State	T_e (cm ⁻¹)	ω_e (cm ⁻¹)	R_e (Å)	B_e (cm ⁻¹)
$X^1\Sigma^-$	0.00 ^a 0.00 ^b	140.22 ^a 151.00 ^b	2.9209 ^a 2.823 ^b	0.0252 ^a 0.0270 ^b
(1) ¹ Σ^+	23391.31 ^a 27493 ^b	40.15 ^a 46.00 ^b	4.100 ^a 3.599 ^b	0.0125 ^a 0.0170 ^b
(1) ¹ Δ	23730.11 ^a 27971.00 ^b	38.90 ^a 41.00 ^b	3.7360 ^a 3.694 ^b	0.0153 ^a 0.0160 ^b
(3) ¹ Δ	23734.06	22.44	4.3691	0.0113
(1) ¹ Δ	23763.11 ^a 28042.00 ^b	37.55 ^a 40.00 ^b	4.2173 ^a 3.748 ^b	0.1103 ^a 0.1500 ^b
(2) ¹ Δ	23763.29 ^a	21.99 ^a	4.4192 ^a	0.0109 ^a
(1) ¹ Σ^-	23881.79 ^a	11.86 ^a	4.6612 ^a	0.0098 ^a
(2) ¹ Σ^-	23886.75 ^a	10.24 ^a	4.9365 ^a	0.0088 ^a
(1) ¹ Σ^-	23888.61 ^a	12.63 ^a	4.6182 ^a	0.0101 ^a
(2) ¹ Δ	23945.91 ^a	29.99 ^a	7.0189 ^a	0.0044 ^a
(3) ¹ Σ^-	25724.64 ^a	38.89 ^a	6.1775 ^a	0.0056 ^a
(3) ¹ Π	42713.81 ^a	38.91 ^a	3.7368 ^a	0.0154 ^a
(3) ¹ Π	43007.26 ^a	19.15 ^a	7.2281 ^a	0.0041 ^a
(4) ¹ Π	50227.78 ^a	49.85 ^a	3.8067 ^a	0.0149 ^a
(4) ¹ Π	50502.01 ^a	52.22 ^a	3.8018 ^a	0.0149 ^a
(2) ¹ Σ^-	64449.87 ^a	103.98 ^a	2.9190 ^a	0.0253 ^a

By comparing our outcomes of spectroscopic constant ω_e with those given in the literature, we obtain a good agreement with the relative differences $\Delta\omega_e/\omega_e = 7.13\%$, $\Delta R_e/R_e = 9.7\%$, and $\Delta B_e/B_e = 0.08\%$ for the ground electronic state $X^1\Sigma^+$ of TII molecule, [4]. These relative differences

become larger for $\Delta\omega_e/\omega_e = 12.7\%$, $\Delta R_e/R_e = 12.0\%$, and in very good agreement with $\Delta B_e/B_e = 0.29\%$ by comparing our values with those of the excited electronic state $(1)^3\Sigma^+$, [4].

Similarly, for $(1)^3\Delta$ electronic state, a strong agreement is obtained between our obtained results and published data for the given spectroscopic constants $\Delta\omega_e/\omega_e = 5.12\%$, $\Delta R_e/R_e = 1.12\%$, and $\Delta B_e/B_e = 4.50\%$. The spectroscopic constants for the other electronic states are not calculated here since they are unbound states, [4].

3.2 Potential Energy Curves

Based on the 21 valence electrons of the Tl atom using the ECP 60 MDF basis set, and the seven valence electrons of the Iodine atom using the ECP46MDF basis set, 16 singlet and triplet electronic states are investigated and plotted in Figure 1 and Figure 2 as a function of internuclear distance R in the ranges $1.8\text{\AA} \leq R \leq 6.80\text{\AA}$ and $2\text{\AA} \leq R \leq 6\text{\AA}$, respectively. The potential energy curves, including spin-orbital coupling, are presented in Figure 3 and Figure 4.

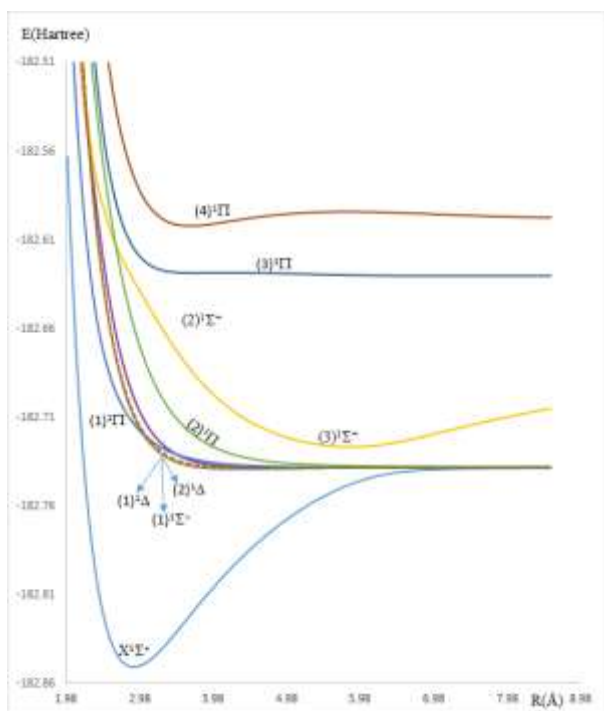


Fig. 1: The potential energy curves of the singlet electronic states of the TII molecule without spin-orbit coupling

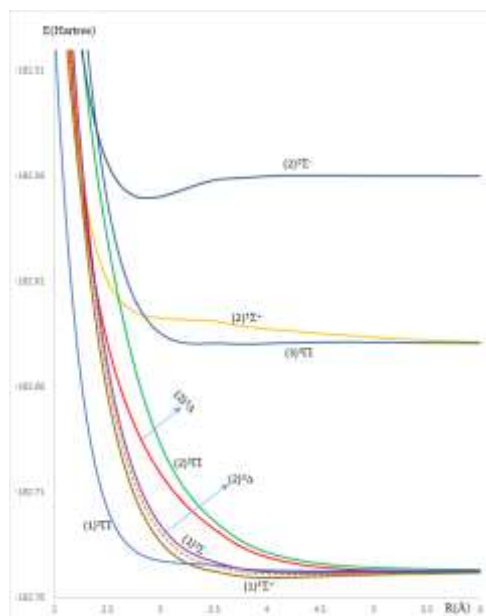


Fig. 2: The potential energy curves of the triplet electronic states of the TII molecule without spin-orbit coupling

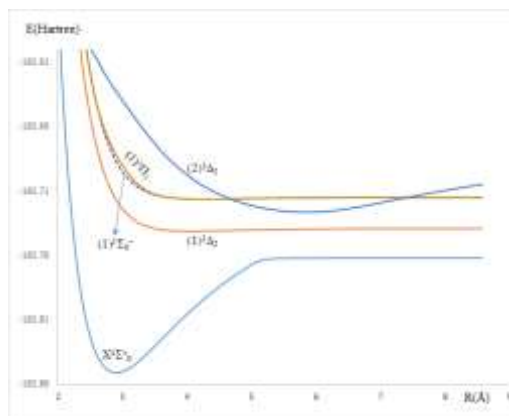


Fig. 3: The potential energy curves of the singlet electronic states of the TII molecule with spin-orbital

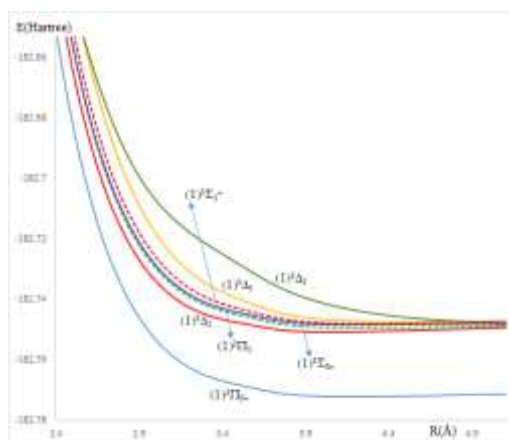


Fig. 4: The potential energy curves of the triplet electronic states of the TII molecule with spin-orbital

The ground state of the considered molecule TII has a deep well, while the other investigated electronic states are shallow or unbound. Mainly most of the studied electronic states reach their dissociation limit at around 5 Å. The potential energy curve's deepness indicates the molecule's stability, while small forces bind the two atoms for a shallow potential energy curve.

To prove the credibility of our investigated values of the TII molecule, we show in Table 3 the trend of the spectroscopic parameters between the TIBr molecule and our obtained values for the TII molecule, [4]. From bromine to iodine in the Periodic Table, the rotational constant B_e decreases as the reduced mass increases. This Table also confirms the increase in bond length R_e and the decrease of harmonic frequency ω_e with the decrease of the electronegativity for all the considered electronic states, which can confirm the reliability of our work.

Table 3. The trend study of the spectroscopic constants of the different electronic states of the molecules TIBr and TII

States	constants	TIBr	TII	trend
$X^1\Sigma^+$	T_e (cm ⁻¹)	0 ^a	0 ^b	↔
	R_e (Å)	2.600 ^a	2.920 ^b	↗
	ω_e (cm ⁻¹)	195.00 ^a	136.00 ^b	↘
	B_e (cm ⁻²)	0.0430 ^a	0.0252 ^b	↘
$(1)^3\Sigma^+$	T_e (cm ⁻¹)	31174.00 ^a	23391.00 ^b	↘
	R_e (Å)	3.483 ^a	4.145 ^b	↗
	ω_e (cm ⁻¹)	53.00 ^a	28.50 ^b	↘
	B_e (cm ⁻²)	0.024 ^a	0.0125 ^b	↘
$(1)^3\Delta$	T_e (cm ⁻¹)	31611.00 ^a	23730.00 ^b	↘
	R_e (Å)	3.570 ^a	37.360 ^b	↗
	ω_e (cm ⁻¹)	47.00 ^a	38.90 ^b	↘
	B_e (cm ⁻²)	0.0234 ^a	0.0153 ^b	↘
$(1)^1\Delta$	T_e (cm ⁻¹)	31664.00 ^a	23763.11 ^b	↘
	R_e (Å)	3.616 ^a	4.4173 ^b	↗
	ω_e (cm ⁻¹)	45 ^a	17.55 ^b	↘
	B_e (cm ⁻²)	0.230 ^a	0.1103 ^b	↘
$(1)^3\Sigma^-$	T_e (cm ⁻¹)	31882.00 ^a	23888.61 ^b	↘
	R_e (Å)	3.654 ^a	4.6182 ^b	↗
	ω_e (cm ⁻¹)	42 ^a	12.63 ^b	↘
	B_e (cm ⁻²)	0.022 ^a	0.0101 ^b	↘
$(1)^3\Sigma^+$	T_e (cm ⁻¹)	31907 ^a	23881.00 ^b	↘
	R_e (Å)	3.666 ^a	4.661 ^b	↗
	ω_e (cm ⁻¹)	42 ^a	11.86 ^b	↘
	B_e (cm ⁻²)	0.022 ^a	0.0098 ^b	↘
$(2)^3\Sigma^+$	T_e (cm ⁻¹)	31932 ^a	23886.75 ^b	↘
	R_e (Å)	3.879 ^a	4.9365 ^b	↗
	ω_e (cm ⁻¹)	33 ^a	10.24 ^b	↘
	B_e (cm ⁻²)	0.020 ^a	0.0088 ^b	↘

^a [4], ^bPresent work

3.3 Permanent Dipole Moment Curves

By taking the iodine atom at the origin, the curves with and without the spin-orbit of the static dipole moment (DMCs) of the TII molecule are plotted as a function of internuclear distance R in Figure 5, Figure 6, Figure 7 and Figure 8. These DMCs are essential in constructing the molecular orbit bonding model, specifying the polarity and the interaction of electronic states, [17], [18], [19]. One can notice that all the investigated DMCs tend to zero at a large

internuclear distance, resulting in a neutral fragment Figure 5 and Figure 8 except for the two electronic states $(3)^1\Sigma^+$ and $(1)^1\Delta_1$. These curves tend to have negative values in the negative region within $5.20\text{Å} \leq R \leq 7.20\text{Å}$ (Figure 5 and Figure 7) where the molecule dissociates in the ionic fragment.

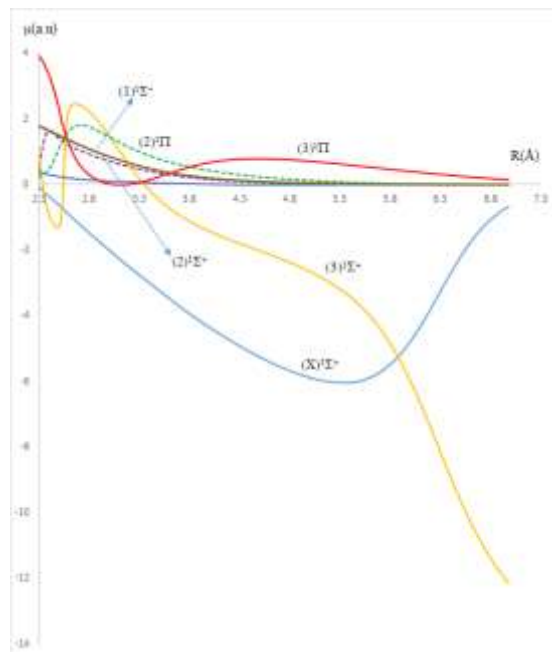


Fig. 5: The dipole moment curves as a function of internuclear distance for the singlet electronic states of TII without spin-orbit coupling

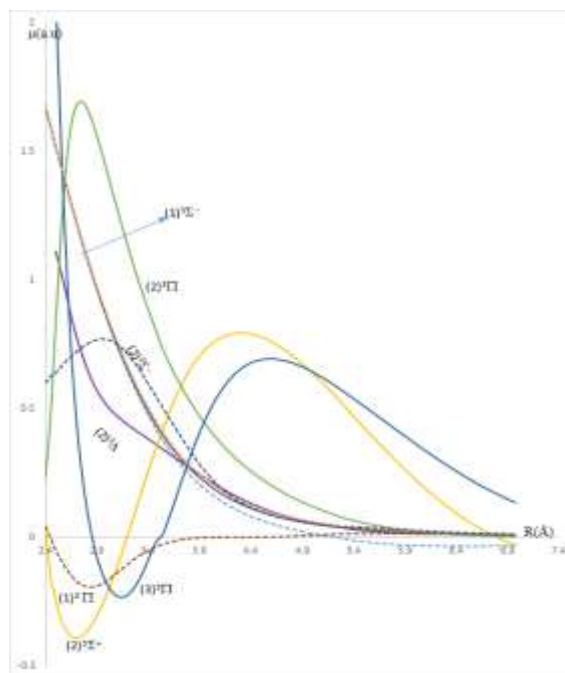


Fig. 6: The dipole moment curves as a function of internuclear distance for the triplet electronic states of TII without spin-orbit coupling

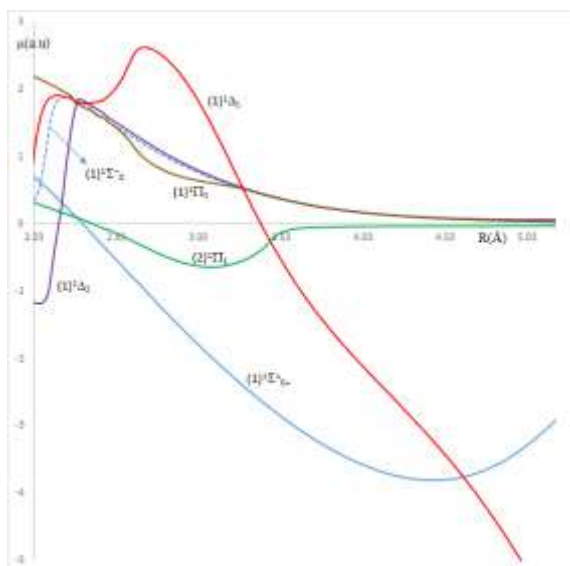


Fig. 7: The dipole moment curves as a function of internuclear distance for the singlet spin-orbit coupling electronic states of the TII molecule

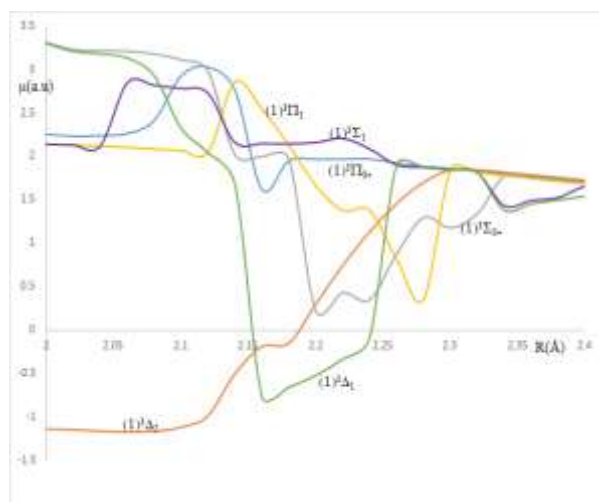


Fig. 8: The dipole moment curves as a function of internuclear distance for the triplet spin-orbit coupling electronic states of the TII molecule

4 Conclusion

Using an ab initio calculation (CASSCF/MRCI + Q) we investigated in the present work the PECs and the DMCs for 19 and 10 electronic states (singlet and triplet) states of TII molecule. In this calculation, the used basis sets are the ECP60MDF [12] and ECP46MDF [13] for Tl and I atoms, respectively. The ground state is confirmed as $X^1\Sigma^+$ with deep potential energy curves for the molecule TII. A good agreement can be noticed by comparing our calculated spectroscopic constants in Table 1 with those in the literature. Our previous work on the iodine compounds confirmed the candidacy of the two molecules CaI and BaI for Doppler laser

cooling. This study of laser cooling for the molecule TII has not been done since the first condition, which is that the small difference between the R_e of the ground and one bound excited state is not verified.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

- Ghina Chamieh: Conception, design, calculation, and writing the paper.
- Lokman Awad: Revising the paper critically for important intellectual content.
- Mahmoud Korek: Supervised and approved the final version.

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Conflict of Interest

The authors declare no competing interests.

Data availability

All data generated or analyzed during this study are included in this published article.

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