Journal of Modern Physics, 2016, 7, 106-113
Published Online January 2016 in SciRes. http://www.scirp.org/journal/jmp
http://dx.doi.org/10.4236/jmp.2016.71010

Ab Initio Calculation of the Electronic States of ScTe Molecule below 19,500 cm^{-1}

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Received 21 November 2015; accepted 18 January 2016; published 22 January 2016

Abstract

The potential energy curves (PECs) of the16 lowest electronic states in the representation $^{2s+1}\Lambda^{(+/-)}$ of the molecule ScTe have been investigated via *ab initio* CASSCF and MRCI (single and double excitations with Davidson correction) calculations. The permanent dipole moment curves (PDMCs) and the spectroscopic constants such as vibrational harmonic frequency ω_e, the internuclear distance at equilibrium R_e, the rotational constant B_e, and the electronic transition energy T_e with respect to the ground state have been calculated for the different bound investigated electronic states. The comparison of the present results with the rare available theoretical data in literature shows an overall good agreement. To the best of our knowledge, 15 electronic states of the ScTe molecule are not yet investigated either experimentally or theoretically, they are investigated in the present work for the first time.

Keywords

***Ab Initio* Calculation, Electronic Structure, Spectroscopic Constants, Potential Energy Curves, Dipole Moments**

1. Introduction

Over the last decade, first principles-based methods (*ab initio* methods) which use only the atomic constants as input parameters for solving the Schrodinger equation have now become the most powerful probes for investigating important number of physical and chemical properties for atoms, molecules and solids. Needless to mention that they are also a tool of choice for the prediction of new materials, and they could sometimes replace experiments which are very costly or even impossible in the laboratory.

The electronic structures and nature of chemical bonds between a transition metal and a main group element

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How to cite this paper: Halabi, R. and Korek, M. (2016) *Ab Initio* Calculation of the Electronic States of ScTe Molecule below 19,500 cm^{-1}. *Journal of Modern Physics*, **7**, 106-113. http://dx.doi.org/10.4236/jmp.2016.71010

are of great interest in many areas of science, e.g., in surface chemistry [1], catalysis [2], astrophysics [3]-[5], organometallic chemistry [6], and high-temperature chemistry [7]. They can also serve as simple models for understanding the properties of more complex transition metal compounds. Scandium is the first transition metal atom which has only one d-electron in the ground state. Diatomic molecules like ScTe are simple transition metal-containing systems in which d-electrons take part in bonding and provide ideal models for understanding the electronic structure and reactivity (chemiluminescent reactions). To the best of our knowledge, no experimental work for the ScTe molecule has been done. The only theoretical work for ScTe in literature is that of Wu *et al.* [8] for the ground $X^2\Sigma^+$ state by using the density functional method DFT-B3LYP technique.

Because of the lack of studies, either theoretical or experimental, for the excited electronic states of the molecule ScTe and based on our previous studies on diatomic molecules especially the scandium compounds ScO [9], ScS [10], ScF [11], ScCl [12], ScBr [13] [14] and ScI [15], we present in this paper *ab initio* investigations of the lowest lying electronic states of the ScTe molecule which have been performed via CAS-SCF/MRCI (Complete Active Space Self Consistent Field, Multireference Configuration Interaction) method. Multireference CI calculations (single and double excitations with Davidson corrections) in which the entire CAS-SCF configuration space was used as the reference were performed to account the correlation effects. The potential energy curves (PECs), the permanent dipole moment curves (DMCs) together with the energy minimum for the ground state $\mathbf{T_e}$, the equilibrium internuclear distance $\mathbf{R_e}$, the harmonic frequency $\boldsymbol{\omega_e}$ and the rotational constant $\mathbf{B_e}$ have been obtained for the 16 lowest-lying electronic states. Fifteen electronic states have been investigated in the present work for the first time. It is hoped that our computational results will stimulate further experimental studies on transition metal diatomic molecules, especially transition metal tellurides.

2. Method of Calculations

In the present work, *ab initio* investigations of the lowest-lying electronic states of the ScSe molecule have been performed via CASSCF method. Multireference MRCI + Q calculations (single and double excitations with Davidson corrections) were performed to determine the correlation effects. The entire CASSCF configuration space was used as a reference in the MRCI calculation which has been performed via the computational chemistry program MOLPRO. The scandium species is treated as a system with 10 inner electrons taken into account using the basis ECP10MDF [16] for s, p and d functions for ScTe. The tellurium atom is treated as a system with 46 inner electrons taken into account using the basis ECP46MWB [17] including s and p functions. In the range of the internuclear distance R_e around equilibrium distances of its ground state, the ScTe molecule is assumed to be mainly ionic as many transition-metals Sc^+Te^-. Among the 73 electrons explicitly considered for ScSe (21 electrons for Sc and 52 for Se) 56 inner electrons were frozen in subsequent calculations so that 17 electrons were explicitly treated. The active space contains 6σ (Sc: 4s; Te: $5p_0$, 6s, $5d_0$, $6p_0$, 7s), 3π (Te: $5p_{\pm1}$, $5d_{\pm1}$, $6p_{\pm1}$) and 1δ (Te: $5d_{\pm2}$), this corresponds to 10 active molecular orbitals in the C_{2v} symmetry distributed into irreducible representation in the following way: $7a_1$, $3b_1$, $3b_2$, $1a_2$, noted [1] [3] [7]. The doubly occupied orbitals 4σ (Sc: 3s, $3p_0$, $3d_0$; Te: 5s), and 2π (Sc: $3p_{\pm1}$, $3d_{\pm1}$) and 1δ (Sc: $3d_{\pm2}$) have been considered as inactive in the CASSCF calculations. Correlation effects for the seven valence electrons have been taken into account through multireference calculations MRCI+Q (single and double excitations with Davidson correction) where the entire CASSCF configuration space has been used as reference. Calculations have been performed via the computational program MOLPRO [18] taking advantage of the graphical user interface GABEDIT [19].

3. Results and Discussion

The potential energy curves for the doublet and quartet electronic states of ScTe molecule in the representation of $^{2s+1}\Lambda^{(+/-)}$ have been calculated in term of the internuclear distance in the ranges $2.00Å \le R \le 3.48Å$ (**Figure 1** and **Figure 2**). The electric dipole moment is a fundamental electrostatic property to study the strength of the long-range dipole-dipole forces, and to understand the macroscopic properties of imperfect gases, liquids and solids. It is demonstrated that the strength of vibrational excitations depends on the variation of the dipole moment as function of geometry such that the DMCs are considered important as they may help to obtain accurate predictions of transition intensities. Hence, the static electric dipole moment of the considered doublet and quartet states are calculated in terms of the internuclear distance R. They will be mainly used here to discuss the bond nature, the polarity and interaction of the electronic states. As the bond nature of an electronic state is related to the magnitude of the dipole moment at a given distance, an ionic nature is indicated from a relatively

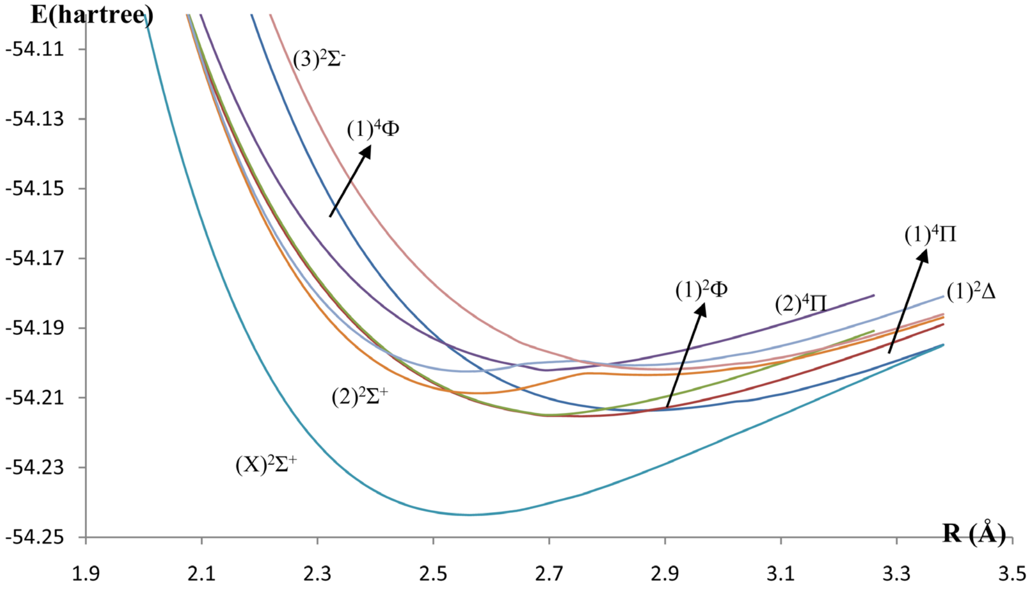

Figure 1. Potential energy curves of the electronic states $X^2\Sigma^+$, (1) $^4\Pi$, (1) $^4\Phi$, (1) $^2\Phi$, (2) $^2\Sigma^+$, (1) $^2\Delta$, (2) $^4\Pi$ and (3) $^2\Sigma^-$ of the molecule ScTe.

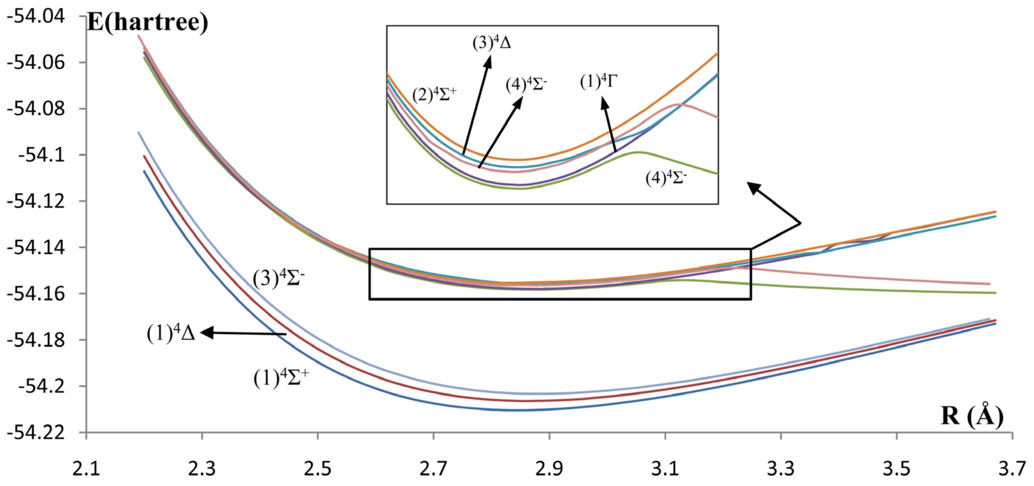

Figure 2. Potential energy curves of the electronic states (1) $^4\Sigma^+$, (2) $^4\Sigma^+$, (3) $^4\Sigma^-$, (4) $^4\Sigma^-$, (1) $^4\Delta$, (2) $^4\Delta$, (3) $^4\Delta$ and (1) $^4\Gamma$ of the molecule ScTe.

large magnitude. It is quite common for the molecular electronic states of the potential energy curves to make crossings or avoided crossings. In fact, the avoided crossing regions are likely to be a leakage channels along which the molecules flow from the higher down to the lower potential energy curves. Such crossings or avoided crossings can dramatically alter the stability of the molecules. If these crossings are overlooked, then low barrier transitions can be missed and an incorrect chemical picture will arise. In the range of R, several avoided crossings have been detected in the potential energy curves for the excited electronic states of the considered molecule ScTe.

For the ScTe molecule, the spectroscopic constants such as the vibration harmonic constant $\boldsymbol{\omega_e}$, the internuclear distance at equilibrium $\mathbf{R_e}$, the rotational constant $\mathbf{B_e}$ and the electronic transition energy with respect to the ground state $\mathbf{T_e}$ have been calculated by fitting the energy values around the equilibrium position to a polynomial in terms of the internuclear distance R. These values are given in **Table 1** together with the available data in the literature.

The only data available in literature for the molecule ScTe are those for the ground state $X^2\Sigma^+$ calculated by

Table 1. Calculated spectroscopic constants for the lowest 16 electronic states of ScTe.

States	T_e (cm^{-1})	R_e (Å)	ω_e (cm^{-1})	$B_e \times 10^2$ (cm^{-1})
$X^2\Sigma^+$	0.0[a] 0.0[b]	2.562[a] 2.496[b]	301.9[a] 341[b]	7.727
$(1)^4\Phi$	6204	2.848	244.3	6.251
$(1)^4\Pi$	6210	2.850	226.8	6.242
$(1)^2\Phi$	6567	2.859	228.4	6.206
$(1)^4\Sigma^+$	7287	2.846	231.9	6.262
$(2)^2\Sigma^+$	7671	2.568	328.1	7.692
$(1)^4\Delta$	8171	2.865	227.2	6.177
$(3)^4\Sigma^-$	8843	2.880	223.3	6.113
$(1)^2\Delta$	9039	2.541	361.9	7.853
$(2)^4\Pi$	9097	2.853	218.1	6.232
$(3)^2\Sigma^-$	9166	2.891	217.7	6.067
$(2)^4\Delta$	18728	2.8719	205.1	6.149
$(1)^4\Gamma$	18814	2.8723	212.2	6.147
$(4)^4\Sigma^-$	19139	2.865	210.6	6.179
$(3)^4\Delta$	19249	2.871	206.1	6.151
$(2)^4\Sigma^+$	19434	2.873	207.7	6.144

[a]Present Theoretical study; [b]Ref [8].

using the DFT-B3LYP technique [8]. The comparison of our investigated values of R_e for the ground states with those given by Wu *et al.* [8] for the considered molecule shows a good agreement with the relative difference $\delta R_e/R_e = 2.6\%$; this agreement becomes larger by comparing our calculated value of ω_e with that given in Ref. [8] with the relative difference $\delta\omega_e/\omega_e = 11.5\%$. No comparisons for the other investigated data for the excited electronic states with other values, since they are given here for the first time.

The dipole moment function of these states exhibits an abrupt changes reflecting the avoided crossing between the two states as also observed at the potential energy curves. The positions of these crossings and avoid crossing are given in **Table 2** and **Table 3**.

In **Figures 3-5** we show the agreement between the positions of the avoided crossings of the PECs and the positions of the crossing of the corresponding DMCs. This agreement can be considered as confirmation of the accuracy of the present results on the ScTe molecule. In the present calculation of the DMCs, we considered the Sc atom at the origin. One can notice that, most of the DMCs for the considered molecule are in the negative regions, where the electronegativity of the Sc atom is higher than those of Te atom in these region and it is independent either on the internuclear distance or the different electronic states. At large internuclear distances the decreased value of the dipole moment can be explained by the polarization of the orbital in the direction of the negatively charged ligand whereas this orbital polarization tends toward the covalent nature for the 2 electronic state (2) $^4\Delta$ and (4) $^4\Sigma^-$ of this molecule.

In **Figure 6**, we show the energy levels $\mathbf{T_e}$ of the investigated molecule ScTe along with those of the molecules ScO [9], ScS [10] and ScSe. By comparing the electronic structure of these molecules one can notice that they all have the same ground state $X^2\Sigma^+$. The order of the electronic states of the considered 4 molecules is disturbed because of the values of the electronegativity of the different investigated electronic states. *i.e.*, the first excited electronic state for the molecules ScO, ScS and ScSe is $(1)^2\Delta$ state while this state for the molecule ScTe is shifted to the 8th excited electronic state **Figure 6**. The values of the dipole moments at the internuclear distances $\mathbf{R_e}$ are 2.41 a.u. and 2.54 a.u. for the ScSe and ScTe molecules respectively which implies higher electronegativity of the ScSe than the ScTe and to the higher electronegative correspond the lower energy. Also, the 2nd excited electronic state for the molecule ScO is (2) $^2\Sigma^+$ state while this state for the molecules ScS, ScSe and ScTe is shifted to the 5th excited electronic state **Table 4**. Similar explanation can be done for other electronic states. Knowing that the electronegativities of Scandium, oxygen, Sulfur, Selenide and that of tellurium atoms are 1.36, 3.44, 2.58, 2.55, and 2.1 respectively [20]. So what it is observed, in **Table 4**, is that when the differ-

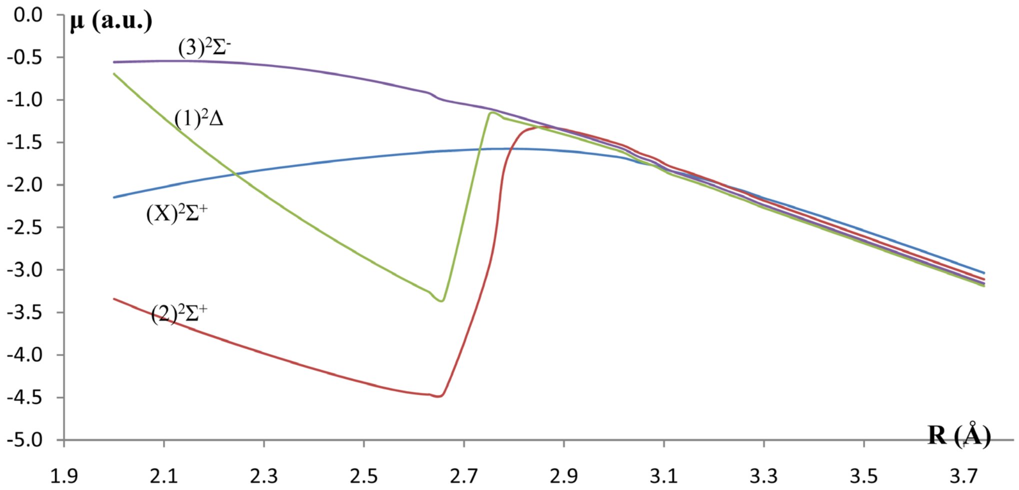

Figure 3. Dipole moment curves of the electronic states $X^2\Sigma^+$, $(1)^2\Delta$, $(2)^2\Sigma^+$ and $(3)^2\Sigma^-$ of the molecule ScTe.

Table 2. Positions of the avoided crossings between the different electronic states (ScTe).

State 1	State 2	Avoided crossing between (n_1) state 1/(n_2) state 2	R_{AC} (Å)	ΔE_{AC} (cm^{-1})
$^4\Delta$	$^4\Delta$	2/3	2.4	608.73
$^4\Delta$	$^4\Delta$	2/3	3.1	665.25

Table 3. Positions of the crossings between the different electronic states (ScTe).

State 1	State 2	Crossing between (n_1) state1/(n_2) state2	R_c(Å)
$^2\Sigma^+$	$^2\Phi$	1/1	3.38
$^2\Sigma^+$	$^4\Pi$	2/1	2.54
$^2\Sigma^+$	$^4\Phi$	2/1	2.54
$^2\Sigma^+$	$^2\Phi$	2/1	2.66
$^2\Delta$	$^4\Phi$	1/1	2.42
$^2\Delta$	$^4\Pi$	1/1	2.42
$^2\Delta$	$^4\Pi$	1/2	2.66
$^2\Delta$	$^2\Phi$	1/1	2.6
$^2\Delta$	$^2\Sigma^-$	1/3	2.75
$^4\Phi$	$^2\Sigma^-$	1/3	3.2
$^4\Phi$	$^2\Phi$	1/1	2.81
$^4\Phi$	$^2\Sigma^+$	1/2	3.11
$^4\Pi$	$^2\Phi$	1/1	2.87
$^4\Pi$	$^2\Phi$	2/1	2.54
$^4\Pi$	$^2\Sigma^-$	2/3	2.78
$^4\Sigma^-$	$^4\Delta$	4/3	3.06
$^4\Sigma^-$	$^4\Gamma$	4/1	3.24
$^4\Sigma^-$	$^4\Delta$	4/3	3.24

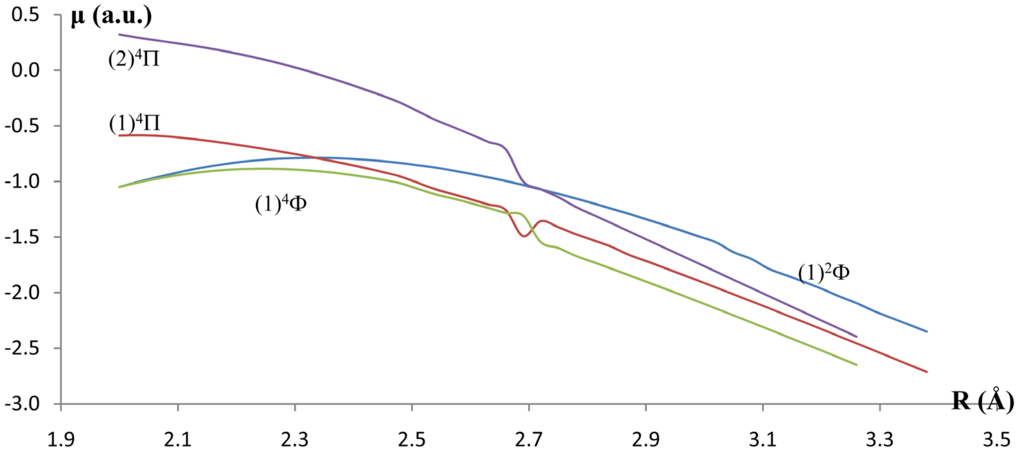

Figure 4. Dipole moment curves of the electronic states $(1)^4\Pi$, $(1)^4\Phi$ and $(2)^4\Pi$ of the molecule ScTe.

Table 4. Values of spectroscopic constants $\mathbf{T_e}$, $\mathbf{R_e}$, $\boldsymbol{\omega_e}$ and $\mathbf{B_e}$ for five different electronic states of the molecules ScO, ScS, ScSe and ScTe.

State	Parametrers	ScO[b]	ScS[a]	ScSe[a]	ScTe[a]	Trend
Electronegativity of the chalcogenides		3.44	2.58	2.55	2.1	↘
Difference in Electronegativity		2.08	1.22	1.19	0.74	↘
$X^2\Sigma^+$	T_e (cm^{-1})	0.0 (GS)	0.0 (GS)	0.0 (GS)	0.0 (GS)	Same GS[*]
	R_e (Å)	1.701	2.181	2.379	2.562	↗
	ω_e (cm^{-1})	1010	540.6	348.7	301.9	↘
	$B_e \times 10^2$ (cm^{-1})	49.39	18.93	10.39	7.73	↘
$(1)^2\Delta$	T_e (cm^{-1})	15,731.3 (1st ES)	8760 (1st ES)	8322 (1st ES)	9039 (8th ES)	Exception
	R_e (Å)	1.777	2.229	2.409	2.541	↗
	ω_e (cm^{-1})	886.1	581.6	401.1	361.9	↘
	$B_e \times 10^2$ (cm^{-1})	45.22	18.13	10.19	7.85	↘
$(2)^2\Sigma^+$	T_e (cm^{-1})	21,071.2 (2nd ES)	11,604 (5th ES)	10,437 (5th ES)	7671 (5th ES)	↘
	R_e (Å)	1.757	2.222	2.399	2.568	↗
	ω_e (cm^{-1})	831.1	557.4	380.5	328.1	↘
	$B_e \times 10^2$ (cm^{-1})	46.27	18.24	10.21	7.69	↘
$(1)^4\Sigma^+$	T_e (cm^{-1})	28,364.8 (6th ES)	12,828 (7th ES)	8486 (2nd ES)	7287 (4th ES)	↘
	R_e (Å)	2.059	2.522	2.695	2.846	↗
	ω_e (cm^{-1})	624.1	350.6	252.8	231.9	↘
	$B_e \times 10^2$ (cm^{-1})	35.46	14.16	8.11	6.26	↘
$(1)^4\Delta$	T_e (cm^{-1})	28,918.2 (7th ES)	13,581 (8th ES)	9339 (3rd ES)	8171 (6th ES)	↘
	R_e (Å)	1.993	2.537	2.713	2.865	↗
	ω_e (cm^{-1})	653.9	344.9	246.5	227.2	↘
	$B_e \times 10^2$ (cm^{-1})	33.85	13.99	7.99	6.18	↘

[*]G.S: Ground State, [*]nth E.S: nth Excited State, [a]Present Theoretical study, [b]Ref. [9].

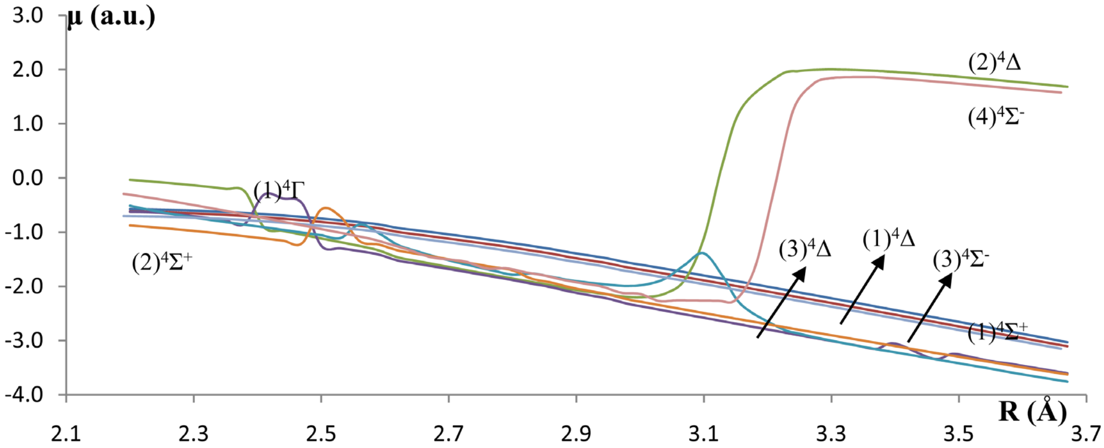

Figure 5. Dipole moment curves of the electronic states (1) $^4\Sigma^+$, (2) $^4\Sigma^+$, (3) $^4\Sigma^-$, (4) $^4\Sigma^-$, (1) $^4\Delta$, (2) $^4\Delta$, (3) $^4\Delta$ and (1) $^4\Gamma$ of the molecule ScTe.

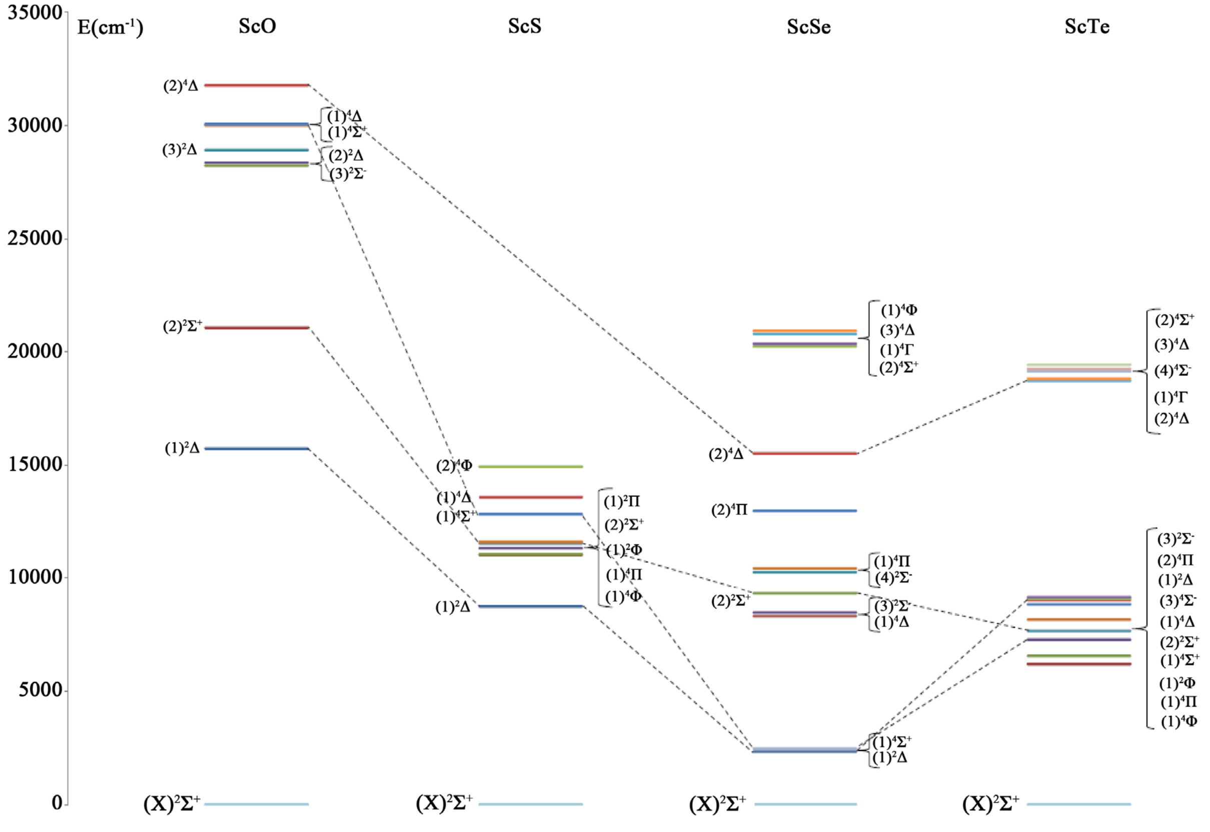

Figure 6. Values of energy levels $\mathbf{T_e}$ for different electronic states of the molecules ScO, ScS, ScSe and ScTe.

ence in electronegativity between (Scandium: Sc) and the (chalcogenide atoms: X = O, S, Se and Te) decreases, the electronic transition energy $\mathbf{T_e}$ with respect to the ground state have decreased. On the other hand, when the equilibrium internuclear distance $\mathbf{R_e}$ increases the harmonic frequency $\boldsymbol{\omega_e}$ decreases and rotational constant $\mathbf{B_e}$ also decreases. This is compatible to the relations between them according to the following equation:

$$B_e = \hbar^2/2I$$

where $I = \mu R^2$. Thus as $\mathbf{R_e}$ increases then rotational constant $\mathbf{B_e}$ decreases.

4. Conclusion

In the present work, the *ab initio* investigation for 16 low-lying electronic states of the ScTe molecule has been performed via CASSCF and MRCI + Q (single and double excitations with Davidson correction) calculations. The calculated potential energy curves, the permanent dipole moment curves, and spectroscopic constants $\mathbf{T_e}$, $\mathbf{R_e}$, $\boldsymbol{\omega_e}$ and the rotational constant $\mathbf{B_e}$ are reported for the 16 lowest electronic states of the molecule ScTe. The overall agreement between our calculated values of the spectroscopic constants for the ground states and those of Wu *et al.* [8] and the agreement between the positions of avoided crossing of the PECs and the crossing of the DMCs for the 15 new excited states may confirm the validity and the accuracy of the present results. These investigated data may help for more experimental or theoretical studies in the future for higher electronic states.

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