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Theoretical investigation of electronic states and spectroscopic properties of tellurium selenide molecule employing relativistic effective core potentials

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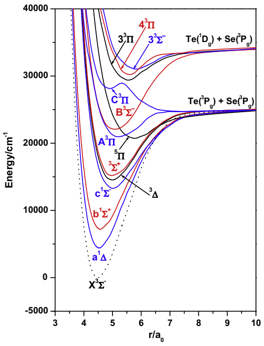
HIGHLIGHTS

- Selection of basis sets and relativistic effective core potentials (RECP) of Te and Se atoms.
- Computation of MRDCI calculations without and with considering effect of spin–orbit coupling.
- Construction of potential energy curves without and with spin–orbit effect.
- Computation of spectroscopic constants without and with spin–orbit effect.
- Computation of transition probabilities of some transitions and dipole moments.

GRAPHICAL ABSTRACT

Potential energy curves of low-lying bound Λ–S states of TeSe.



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ABSTRACT

Ab initio based relativistic configuration interaction calculations have been performed to study the electronic states and spectroscopic properties of tellurium selenide (TeSe) – the heaviest heteronuclear diatomic group 16–16 molecule. Potential energy curves of several spin-excluded (Λ–S) electronic states of TeSe have been constructed and spectroscopic constants of low-lying bound Λ–S states within 3.85 eV are reported in the first stage of calculations. The $X^3\Sigma^-$, $a^1\Delta$ and $b^1\Sigma^+$ are found as the ground, first excited and second excited state, respectively, at the Λ–S level and all these three states are mainly dominated by $\ldots\pi^4\pi^{*2}$ configuration. The computed ground state dissociation energy is in very good agreement with the experimental results. In the next stage of calculations, effects of spin–orbit coupling on the potential energy curves and spectroscopic properties of the species are investigated in details and compared with the existing experimental results. After inclusion of spin–orbit coupling the $X_1^3\Sigma_{0^+}^-$ is found as the ground-state spin component of TeSe. The computed spin–orbit splitting between two components of $X^3\Sigma^-$ state is 1285 cm^{-1}. Also, significant amount of spin–orbit splitting are found between spin–orbit components (Ω-components) of several other excited states. Transition moments of some important spin-allowed and spin-forbidden transitions are calculated from configuration interaction wave functions. The spin-allowed transition $B^3\Sigma^-$–$X^3\Sigma^-$ and spin-forbidden transition $b^1\Sigma_{0^+}^+$–$X_1^3\Sigma_{0^+}^-$ are found to be the strongest in their respective categories. Electric dipole moments of all the bound Λ–S states along with those of the two Ω-components of $X^3\Sigma^-$ are also calculated in the present study.

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Introduction

The tellurium selenide (TeSe) is a diatomic molecule containing atoms of group VIA and it is the heaviest heteronuclear diatomic group 16–16 molecule. It is one of the molecules belonging to the group VIA whose ground state $^3\Sigma^-$ splits into two widely separated components $X^3_1\Sigma^-_{0^+}$ and $X^3_2\Sigma^-_1$ by application of spin–orbit interaction. This intermetallic dimer is a photoconducting semimetal material and is widely used for preparation of optoelectronic devices such as liquid crystal light waves (LCLV) [1]. In recent years, researchers [2] are very much interested in preparation of nanowires, nanotubes and semiconductor heterojunction nanorods from this material as well as in their studies and applications.

There are very few experimental spectroscopic studies [3–12] available for this species while no theoretical study has yet been performed to investigate the electronic states and spectroscopic properties of this molecule. The thermochemical data for the dissociation energy of few diatomic selenides (BiSe and TeSe) and tellurides (BiTe and SbTe) from the reaction $M_2(g) + Y_2(g) = 2MY(g)$ was reported for the first time by Porter and Spencer [3] using mass spectrometric technique. In their study, M–Y systems were taken as Bi–Se, Bi–Te, Sb–Te and Te–Se. From their study, they have reported the ground-state dissociation energy for TeSe as 3.0 eV. Joshi and Sharma [4] have observed the violet degraded bands of this species in absorption in the quartz ultra-violet region 2520–2140 Å, classified most of the bands into two systems and found the vibrational constants such as transition energies (T_e), vibrational frequencies (ω_e) and first anharmonicity constants ($\omega_e x_e$) of these two systems.

Ahmed and coworkers [5] have observed and analyzed the fluorescence spectra of gaseous, isotopically pure samples of TeSe by exciting it with five lines of argon ion laser. They photographed the D–X systems of ^{128}Te^{78}Se in absorption at moderate resolution and confirmed that the ground state of this molecule is mainly represented by $\ldots\sigma^2\pi^4\pi^{*2}$ ($^3\Sigma^-$) configuration. They have analyzed twenty-one fluorescence series for $B0^+$–$X0^+$, $A0^+$–$X0^+$, B1–X1 c1–X1 and $B0^+$–X1 systems of ^{128}Te^{78}Se, ^{128}Te^{80}Se, ^{130}Te^{78}Se, and ^{130}Te^{80}Se isotopologues and reported molecular constants such as T_e, ω_e and $\omega_e x_e$ for ground-state spin components ($X_1 0^+$ and $X_2 1$) as well as for the excited states components $A0^+$, $B0^+$, B1 and c1 of these species. Their study has revealed the energy separation between the ground-state spin components of ^{128}Te^{78}Se as 1547.2 cm^{-1}. Study of laser induced fluorescence spectra of both natural and isotopically enriched samples of Te_2, TeS, SeS and TeSe in their vapor phase and argon matrices have also been reported by Ahmed and Nixon [6]. They have observed nine band systems for each of the four molecules. They have reported molecular constants such as T_e, ω_e and $\omega_e x_e$ for ground and some low-lying excited states of ^{130}Te$_2$, ^{130}Te^{32}S, ^{78}Se^{32}S and ^{128}Te^{80}Se in both their vapor phases and argon matrices. From their study, the energy splitting between the ground state spin components of ^{128}Te^{80}Se in its vapor phase is found to be almost similar to that of ^{128}Te^{78}Se reported by Ahmed and coworkers [5].

Drowart and Smoes [7] have derived the thermodynamic properties of TeSe from Knudsen-cell mass spectrometric experiments. From their study, they have reported the ground-state dissociation energy of TeSe as 3.0398 eV. Winter and coworkers [8] have observed near-infrared emissions of the $b0^+$–$X_1 0^+$, $X_2 1$ band systems of TeSe in a discharge flow system. From the analysis of the spectra, they have reported $T_e = 8794 \pm 5$ cm^{-1} and $\omega_e = 294 \pm 3$ cm^{-1} for $b0^+$ state. They have also reported the energy splitting between the ground state spin components as 1235 ± 5 cm^{-1}. Fink and coworkers [9] have observed the rotationally resolved IR-chemiluminescence spectrum of TeSe in its gaseous state. They have recorded the 0–0 band of the $b0^+$–$X_1 0^+$ subsystem at very high resolution using separated ^{130}Te and ^{80}Se isotopes and carried out their rotational analysis. They have reported several molecular constants, mainly r_e, ω_e and $\omega_e x_e$, of both the $X_1 0^+$ and $b0^+$ states for the species ^{130}Te^{80}Se from the rotational analysis of the 0–0 band.

The Fourier transform infrared magneto-optical spectrum of the Se_2, Te_2 and TeSe at a temperature 4 K in rare gas matrices have been studied by Li and coworkers [10]. They have observed the spectrum of the zero-field X1–$X0^+$ band of TeSe molecule in rare-gas matrices at 4 K temperature with 0, 2 and 4 Tesla magnetic field strengths. From their study, they have and reported the energy splitting between the ground state spin components of TeSe as 1243 ± 2 cm^{-1}, 1248 ± 2 cm^{-1} and 1234 ± 2 cm^{-1} in krypton (Kr), argon (Ar) and neon (Ne) matrices, respectively, and compared them with the corresponding gas-phase value, reported by Winter and coworkers [8].

Banser and coworkers [11] have designed a new twin laser-ablation source and shown that the combination of supersonic jet Fourier transform microwave (FTMW) spectroscopy and the laser-ablation is a very powerful tool for research on intermetallic species. With this combination of techniques, they have investigated the spectroscopic parameters, structural information, internuclear potential, electronic structure and details of the chemical bond of TeSe from high-resolution multi-isotopologue pure rotational spectra. They have reported vibrational ground-state constants such as equilibrium bond length (r_e) and ground-state dissociation energy (D_e), vibrational frequency (ω_e) and first anharmonicity constant ($\omega_e x_e$), of the main and most abundant isotopologue ^{130}Te^{80}Se considering Morse potential function.

In a subsequent article [12], Banser and coworkers have analyzed the pure rotational spectrum of TeSe in its $X0^+$ electronic ground state by a global multi-isotopologue Dunhum fit. From their analysis, they have derived the rotational and vibrational parameters for 43 TeSe isotopologues. They have reported isotopologue independent ground-state molecular constants such as equilibrium bond length (r_e) and ground-state dissociation energy (D_e) of TeSe using Morse potential function. They have also reported the fundamental vibrational frequencies (ω_e) and first anharmonicity constants ($\omega_e x_e$) of ^{128}Te^{78}Se, ^{128}Te^{80}Se and ^{130}Te^{80}Se isotopologues.

In this article, we have provided a detailed theoretical study of the electronic states and spectroscopic properties of TeSe using ab initio based configuration interaction (CI) methodology which includes relativistic effects and spin–orbit coupling. Potential energy curves of the ground and low-lying excited spin-excluded (Λ–S) and spin-included (Ω) states of TeSe are constructed. Spectroscopic parameters in both the cases are calculated and compared with the existing experimental data. Transition dipole moments of some important dipole-allowed and spin forbidden transitions are computed and from these data we have calculated radiative lifetimes of some excited states at the lowest three vibrational levels. In the present article, we have also computed the *z*-component of electric dipole moments (μ_z) of all the bound Λ–S states as well as two Ω-components ($\Omega = 0^+, 1$) of the ground state as a function of bond distance and reported their value $(\mu_z)_{eq}$ at respective equilibrium of all these states.

Computational details

As both the tellurium (Te) and selenium (Se) atoms are fairly heavy, the use of relativistic effective core potentials (RECP) is appropriate in the present configuration interaction (CI) calculations. The $4d^{10}5s^25p^4$ electrons of Te are kept in valence space and allowed to take part in CI calculations while its 36 core electrons, described by $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$, are substituted by semi-core type RECPs of LaJohn and coworkers [13]. The