Low-lying Electronic States of GeSe: Multireference Singles and Doubles Configuration Interaction Study

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Several low-lying electronic states of GeSe up to the energy of 36 000 cm^{-1} have been studied by using the ab initio-based multireference singles and doubles configuration interaction calculations which include relativistic effective core potentials. Potential energy curves of 18 Λ−S states which dissociate into the ground-state limit Ge(^3P_g)+Se(^3P_g) have been computed. Effects of spin−orbit coupling on these states are also studied. We have also computed potential energy curves of bound Ω-states arising from those 18 Λ−S states within the energy limit of 31 000 cm^{-1}. Spectroscopic constants (r_e, T_e, ω_e, and β_e) at equilibrium of all bound states are estimated. The ground state of GeSe is X0$^+$ ($^1\Sigma^+$) originating mainly from $\sigma^2\sigma^2\sigma^2\pi^4$ and $\sigma^2\sigma^2\sigma^2\pi^3\pi$ configurations with $r_e = 2.172$ Å, $\omega_e = 382$ cm^{-1}, and $\beta_e = 0.093$ cm^{-1}. The agreements with the available experimental values are fairly good. The spin−orbit interactions have little effects on the composition of the low-lying states. The transition energy of the observed A1($^1\Pi$) ← X0$^+$ ($^1\Sigma^+$) transition agrees well with the calculated value. The lifetimes of the excited A$^1\Pi$ and 2$^1\Sigma^+$ states are estimated to be 0.42 and 0.45 μs, respectively.

I. Introduction

The ultraviolet absorption spectra of a series of diatomic molecules formed by the Ge atom and group VIB atom have been studied long ago by Barrow and co-workers.[1,2] Each of the molecules GeO, GeS, GeSe, and GeTe shows a stong band of the type D−X in the UV region. Some weak bands of the type E−X for GeO, GeSe, and GeTe have also been detected. These molecules are found to have $^1\Sigma^+$ as the ground state. The vibrational analyses of the D−X system of GeSe and GeTe have been carried out from the measurements of the spectra emitted by the high-current positive-column discharges.[1] The v′(0,0) band of the D−X system of GeSe is assigned in the region of 30 776 cm^{-1}. However, the D−X system has been reassigned as the A$^1\Pi$ −X$^1\Sigma^+$ band.[3] It is important to know the probability of the A$^1\Pi$ −X$^1\Sigma^+$ transition and hence the lifetime of the upper A state. No experimental results are available on this aspect. The rotational constants and equilibrium bond lengths of different isotopomers of GeSe have been obtained from the microwave spectrum observed by Hoeft.[4] Several other rotational and vibrational spectra have been observed experimentally.[5,6] Very recently, infrared diod laser spectroscopy of this high-temperature molecule GeSe has been carried out by Konno and Uehara.[7] The vibrational analyses of the upper states have become useful in identifying the dissociation limits of these compounds. For GeSe, the dissociation energy of the E state derived from the vibrational analyses[2] is found to be 0.84 eV and, at the dissociation limit, the products are predicted to be Ge(^3P) + Se(^3P). The ground state of these compounds dissociates into Ge($^3P_0$) + X($^3P_2$) (X = O, S, Se, and Te). However, for this upper state E, the dissociation limit could not be predicted with certainty. The dissociation energy of the ground-state X$^1\Sigma^+$ of GeSe has been given a tentative value of 4.98 ± 0.25 eV.[2] Theoretical calculations on these molecules of germanium have not been carried out so far. Using the relativistic effective core potential (RECP) method in conjunction with the spin−orbit configuration interaction (CI) calculations, it has now become possible to investigate the electronic spectra of these molecules much accurately. In the present calculation, we have computed the potential energy curves of low-lying electronic states of GeSe. Effects of the spin−orbit coupling on the spectroscopic parameters of the low-lying states of GeSe have also been studied. The transition probabilities of several transitions from A$^1\Pi$ and 2$^1\Sigma^+$ and hence lifetimes of these two upper states are estimated from the CI calculations.

II. Computational Methods

The outermost 4s^{2}4p^2 electrons of Ge and 4s^{2}4p^4 electrons of Se are kept in the valence space while the remaining inner electrons are replaced by the full-core RECPs taken from Hurley et al.[8] For both Ge and Se, we have chosen (3s3p) primitive Gaussian type of basis sets.[8] These basis sets of Hurley et al. are augmented with a set of d-polarization functions with exponents ζ_d (Ge) = 0.2 and ζ_d (Se) = 0.25 taken from earlier works of Balasubramanian on Ge$_2$ and Se$_2$ molecules.[9−11] In the first step, a self-consistent field (SCF) calculation is carried out for the ...$\pi^2\pi^2$ $^5\Sigma^+$ state with 10 valence electrons at each internuclear distance. The resulting SCF MOs are used as one-electron functions for the CI treatment for a large number of electronic states. There are 10 electrons in the active space in the CI calculations. The multireference singles and doubles CI (MRDCI) method[12−15] is employed for the calculations of Λ−S states without spin−orbit coupling but with the inclusion of other spin independent relativistic effects. The CI codes of Buenker and co-workers,[12−15] which use the Table CI algorithm[16,17] to handle open-shell configurations efficiently, have been used in this calculation. Several important reference configurations are defined for low-lying excited states of a given Λ −S symmetry. All singly and doubly excited configurations are generated from

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TABLE 1: Correlation between the Atomic States in the Dissociation Limit and Molecular (Λ−S) States of GeSe without Spin−Orbit Interaction[a]

Λ−S states	atomic states in the dissociation limits	experimental energy (cm^{-1})
$^1\Sigma^+(2)$, $^1\Sigma^-$, $^1\Pi(2)$, $^1\Delta$, $^3\Sigma^+(2)$, $^3\Sigma^-$, $^3\Pi(2)$, $^3\Delta$, $^5\Sigma^+(2)$, $^5\Sigma^-$, $^5\Pi(2)$, $^5\Delta$	$^3P_g(Ge)+^3P_g(Se)$	0
$^3\Sigma^+$, $^3\Sigma^-(2)$, $^3\Pi(3)$, $^3\Delta(2)$, $^3\Phi$	$^1D_g(Ge)+^3P_g(Se)$	7126
$^3\Sigma^+$, $^3\Sigma^-(2)$, $^3\Pi(3)$, $^3\Delta(2)$, $^3\Phi$	$^3P_g(Ge)+^1D_g(Se)$	9576
$^1\Sigma^+(3)$, $^1\Sigma^-(2)$, $^1\Pi(4)$, $^1\Delta(3)$, $^1\Phi(2)$, $^1\Gamma$	$^1D_g(Ge)+^1D_g(Se)$	16702

[a] Moore's table [ref 20].

these reference configurations. A perturbative scheme is employed to reduce the size of the secular equations. The energy extrapolation technique along with the Davidson correction[18,19] gives an accurate estimate of the full CI results in the same AO basis. In the present calculations, we have chosen a configuration selection threshold of 20 μhartree. The actual calculations have been carried out in the C_{2v} subgroup for simplicity. However, the corresponding $C_{\infty v}$ notations for different roots of a particular irreducible representation are identified. The resulting CI wave functions are used to compute the one-electron property matrix elements. The electric dipole transition moments are calculated between pairs of Λ−S variational CI wave functions which are nonzero by symmetry. These results are fitted into polynomials and averaged over pairs of vibrational functions involved in a given electronic transition. The resulting vibrational matrix elements are then employed to calculate individual Einstein spontaneous emission coefficients. The radiative lifetimes of excited vibrational levels are computed by summing over their respective transition probabilities to all lower lying states and then inverting the total transition probabilities. In the present calculation we have focused on two excited states $A^1\Pi$ and $2^1\Sigma^+$ for estimating their radiative lifetimes.

III. Discussion of the Calculated Results

Λ−S Potential Energy Curves. The combination of the ^3P_g ground state of both Ge and Se generates 18 states of singlet, triplet, and quintet multiplicities. In Table 1, we have given the dissociation limits and their correlation with the corresponding molecular states without any spin−orbit interaction. Several very high-energy states correspond to the dissociation limit in which one of the two atoms is in the ground state and the other in the first excited state ^1D_g. In the present study we are confined with the lowest dissociation limit only. Potential energy curves of all 18 Λ−S states of GeSe dissociating into Ge(^3P_g) + Se(^3P_g) are shown in Figure 1 in which all the relativistic effects except the spin−orbit coupling are included in the Hamiltonian. The calculated spectroscopic constants of eleven bound states of GeSe are listed in Table 2. The remaining seven states are repulsive in nature. The ground state is definitely $^1\Sigma^+$. The equilibrium bond length of the ground state is 2.17 Å compared with the experimental value of 2.135 Å. Other spectroscopic constants also agree with the available experimental results. The ground-state wave function is dominated by the closed shell configuration ...$\sigma_1^2\sigma_2^2\sigma_3^2\pi^4$. However, some contributions come from the open-shell configurations like ...$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ and ...$\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^4$. Table 3 displays the dominant configurations of all bound Λ−S states of GeSe at their equilibrium geometries. The single excitation $\pi^4 \rightarrow \pi^3\pi$ generates six states of Σ^+, Σ^-, and Δ symmetries of which three are singlets and the remaining three are of the triplet multiplicity. $^3\Sigma^+$ is the first excited state of GeSe with about 75% contribution from ...$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ configuration (see Table 3). It is lying 17 890 cm^{-1} above the ground state and the bond length is somewhat longer than the ground-state r_e because of the dominant open-shell configuration. The same $\pi^4 \rightarrow \pi^3\pi$ excitation generates a $^3\Delta$ state in the region of 20 856 cm^{-1}. Three other Λ−S states, namely, $^1\Sigma^-$, $^3\Sigma^-$, and $^1\Delta$ are nearly degenerate around 22 500 cm^{-1} and all of them are described

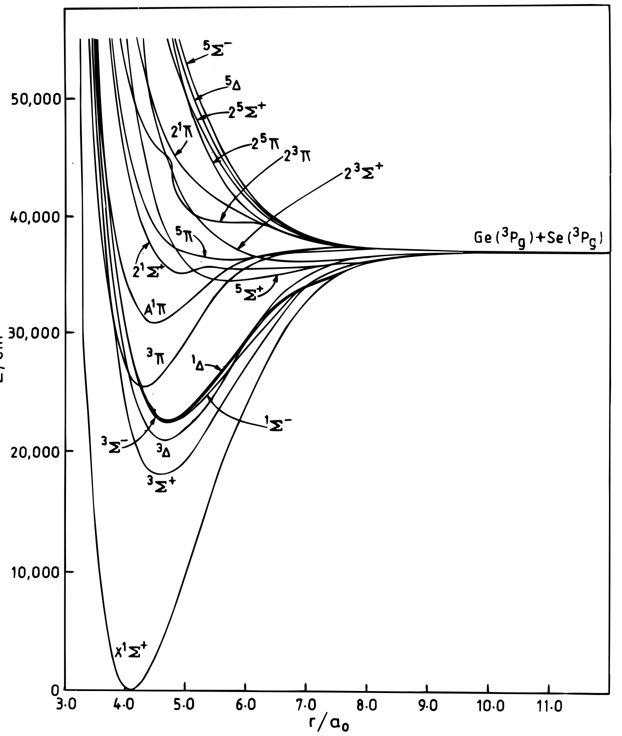

Figure 1. Potential energy curves of 18 Λ−S states of GeSe.

TABLE 2: Spectroscopic Constants of the Bound Λ−S States of GeSe[a]

state	T_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})	β_e(cm^{-1})
$X^1\Sigma^+$	0	2.170 (2.135)	384 (409)	0.093 (0.096)
$^3\Sigma^+$	17 890	2.441	251	0.074
$^3\Delta$	20 856	2.473	247	0.072
$^1\Sigma^-$	22 503	2.514	230	0.070
$^3\Sigma^-$	22 535	2.490	238	0.071
$^1\Delta$	22 570	2.504	250	0.071
$^3\Pi$	25 528	2.275	320	0.085
$A^1\Pi$	30 794 (30 846)	2.383	259 (269)	0.077
$^5\Sigma^+$	34 380	3.116	106	0.045
$2^1\Sigma^+$	35 052	2.618	222	0.065
$^5\Pi$	36 265	3.079	112	0.046

[a] Values in parantheses are taken from the experiment [ref 2].

TABLE 3: Main Electronic Configurations of the Low-lying Bound Λ−S States of GeSe at Their Equilibrium Internuclear Distances

state	configurations (percentage contributions)
$X^1\Sigma^+$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^4$ (52), $\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (30), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^4$ (4)
$^3\Sigma^+$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (75), $\sigma_1^2\sigma_2^2\sigma_3^2\pi^2\pi^2$ (10), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^3\pi$ (5)
$^3\Delta$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (79), $\sigma_1^2\sigma_2^2\sigma_3^2\pi^2\pi^2$ (5), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^3\pi$ (5)
$^1\Sigma^-$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (80), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^3\pi$ (6)
$^3\Sigma^-$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (80), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^3\pi$ (5)
$^1\Delta$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (81), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^3\pi$ (6)
$^3\Pi$	$\sigma_1^2\sigma_2^2\sigma_3\pi^4\pi$ (60), $\sigma_1^2\sigma_2^2\sigma_3\pi^3\pi^2$ (19), $\sigma_1^2\sigma_2\sigma_3^2\pi^4\pi$ (7)
$A^1\Pi$	$\sigma_1^2\sigma_2^2\sigma_3\pi^4\pi$ (55), $\sigma_1^2\sigma_2^2\sigma_3\pi^3\pi^2$ (16), $\sigma_1^2\sigma_2\sigma_3^2\pi^4\pi$ (13)
$2^1\Sigma^+$	$\sigma_1^2\sigma_2^2\sigma_3^2\pi^2\pi^2$ (43), $\sigma_1^2\sigma_2^2\sigma_3\sigma_4\pi^4$ (17), $\sigma_1^2\sigma_2^2\sigma_3^2\pi^4$ (13), $\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (10)

mainly by the configuration ...$\sigma_1^2\sigma_2^2\sigma_3^2\pi^3\pi$ (80%). The equilibrium vibrational frequencies of these excited states are somewhat smaller compared with the ground state ω_e. The lowest $^3\Pi$ state has somewhat shorter bond length with r_e = 2.275 Å as calculated in the present study. Near the minimum of the potential energy curve, the CI wave function of this state is dominated by ...$\sigma_1^2\sigma_2^2\sigma_3\pi^4\pi$ along with some contribution from ...$\sigma_1^2\sigma_2^2\sigma_3\pi^3\pi^2$. The transition energy of this $^3\Pi$ state is calculated to be 25 528 cm^{-1}, and it is relatively strongly bound with ω_e = 320 cm^{-1}. The higher $2^3\Pi$ state is repulsive in nature and it dissociates into the same ^3P_g +^3P_g limit. As seen from the potential energy curves in Figure 1 there exists an avoided crossing at around 4.7 a$_o$ between the two higher $^3\Pi$ states arising from two different configuartions. At the bond length above r = 4.7 a$_o$, the $2^3\Pi$ state is described by ...$\sigma_1^2\sigma_2^2\sigma_3^2\sigma_4\pi^3$ while in the lower bond length region it is dominated by...$\sigma_1^2\sigma_2^2\sigma_3\pi^3\pi$.[2] Next important excited state is the lowest $^1\Pi$ state, which is designated as the A state.[3] However, it is the same D state as denoted by Barrow and co-workers.[1,2] From the symmetry point of view $A^1\Pi \leftrightarrow X^1\Sigma^+$ is an allowed perpendicular transition. In our calculation, the $A^1\Pi$ state lies 30 794 cm^{-1} above the ground state with r_e = 2.383 Å and ω_e = 259 cm^{-1}. Experimentally,[3] the A−X band has been observed at around 30 846 cm^{-1}, which is in excellent agreement with the calculated value. The observed vibrational frequency also agrees well. The $2^1\Pi$ state which dissociates into the same atomic states is purely repulsive. The excited $2^1\Sigma^+$ state is weakly bound. The depth of the potential well is very low, and there exists only three vibrational levels. The CI estimated transition energy of this state is 35 052 cm^{-1} with a longer bond length r_e = 2.618 Å and smaller ω_e = 222 cm^{-1}. The CI wave function of this state is dominated by the configuration ...$\sigma_1^2\sigma_2^2\sigma_3^2\pi^2\pi^2$. Three other important configurations contribute in this state as seen from Table 3. There are six quintet states which dissociate into the lowest limit ^3P_g + ^3P_g. The $^5\Sigma^+$ and $^5\Pi$ states have a very shallow potential well (see Figure 1). The estimated spectroscopic constants are listed in Table 2. Both of these quintet states have comparatively longer bond lengths (Å), and ω_e is only around 100 cm^{-1}. The transition energy of the $^5\Sigma^+$ state is about 34 380 cm^{-1} while the $^5\Pi$ state is lying around 36 265 cm^{-1}. Other four quintet states, namely, $2^5\Sigma^+$, $^5\Delta$, $^5\Sigma^-$, and $2^5\Pi$, are repulsive in nature. The ground-state dissociation energy estimated from the MRDCI calculation is found to be about 4.6 eV compared with the experimental value of 4.98 ± 0.25 eV.[2] For the excited $A^1\Pi$ state, the calculated dissociation energy is 0.75 eV.

TABLE 4: Correlation between the Atomic and Molecular States of the Low-lying States of GeSe with Spin−Orbit Coupling[a]

Ω-states	atomic states in the dissociation limits	experimental energy (cm^{-1})
0^+, 1, 2	$^3P_0$ (Ge)+$^3P_2$ (Se)	0
0^+, 0^- (2), 1(3), 2(2)	$^3P_1$ (Ge) + $^3P_2$ (Se)	557
0^+ (3), 0^- (2), 1(4), 2(3), 3(2), 4	$^3P_2$ (Ge) + $^3P_2$ (Se)	1410
0^-, 1	$^3P_0$ (Ge) + $^3P_1$ (Se)	1990
0^+	$^3P_0$ (Ge) + $^3P_0$ (Se)	2534
0^+ (2), 0^-, 1(2), 2	$^3P_1$ (Ge) + $^3P_1$ (Se)	2547
0^-, 1	$^3P_1$ (Ge) + $^3P_0$ (Se)	3091
0^+, 0^- (2), 1(3), 2(2), 3	$^3P_2$ (Ge) + $^3P_1$ (Se)	3400
0^+, 1, 2	$^3P_2$ (Ge) + $^3P_0$ (Se)	3944

[a] Moore's table [ref 20].

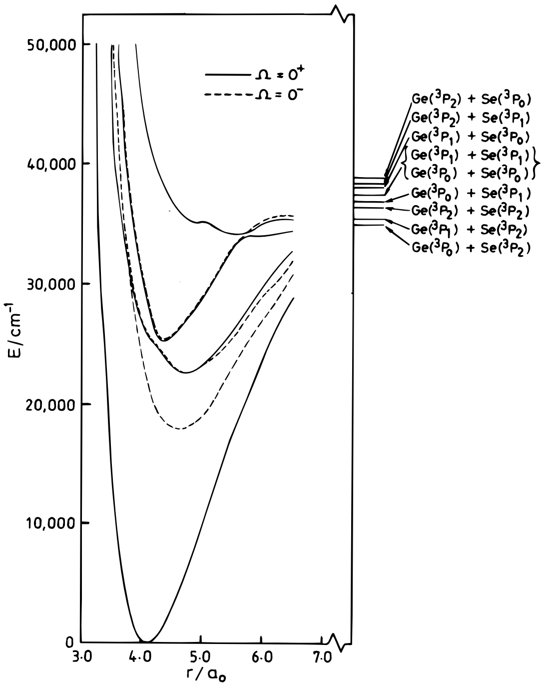

Figure 2. Potential energy curves of low-lying Ω = 0^+ and 0^- states of GeSe.

Inclusion of the Spin−Orbit Coupling. The introduction of the spin−orbit interaction through RECPs leads to a mixing of various Λ−S states. In the present study we have focused on those Ω-states, which are obtained from the mixing of 18 low-lying Λ−S states correlating the ground-state atomic limit ^3P_g + ^3P_g. We have included all 18 states in the super CI calculations. In Table 4, we have tabulated all possible Ω-states along with their dissociation limits and experimental energy values.[20] Nine asymptotes are very closely spaced and correlate with 49 Ω-states. There are 10 states of 0^+ and nine states of 0^- symmetries, 16 states with Ω = 1, 10 states with Ω = 2, 3 states with Ω = 3 and 1 state with Ω = 4. In Figures 2−4, we have plotted the potential energy curves of the bound Ω-states. The estimated spectroscopic parameters of these states lying below 31 000 cm^{-1} are listed in Table 5. The ground-state X0^+ is dominated by $^1\Sigma^+$. Spectroscopic constants change insignificantly due to the spin−orbit interaction. The $^3\Sigma^+$ state splits in the usual manner with the component Ω = 1 lying lower than the 0^- component by about 265 cm^{-1}. The component 0^- is almost pure with 99% contribution from $^3\Sigma^+$ while the component 1 is composed of 92.9% $^3\Sigma^+$ and 6.8% $^3\Sigma^-$. Three components of $^3\Delta$ come next. The component with Ω = 2 lies below the other two components due to a significant spin−orbit interaction and it is composed of $^3\Delta$ (78%) and $^1\Delta$ (22%) while the components with Ω = 1 and 3 remain almost pure $^3\Delta$. The second 0^+ state is described mainly by $^3\Sigma^-$ with 1.5% contribution from the $^3\Pi$ state. The third state with Ω = 1 is dominated by $^3\Sigma^-$ along with 6.5% contribution from $^3\Sigma^+$. The two components of $^3\Sigma^-$ are separated by about 330 cm^{-1}. The 0^- ($^1\Sigma^-$) state lies between them. The state with Ω = 2 arising from 77% $^1\Delta$, 21% $^3\Delta$, and 2% $^3\Pi$ comes next in the energy ordering. All four components of $^3\Pi$ get mixed up with other Λ−S states. The spin−orbit effects on these states are considerably large as seen from r_e and ω_e values in Tables 2 and 5. The 0^+ ($^3\Pi$) state is described by 86% $^3\Pi$ and 14% $^3\Sigma^-$, while 0^- ($^3\Pi$) is a mixture of 78% $^3\Pi$, 20% $^1\Sigma^-$, and 1% $^3\Sigma^+$. The fourth Ω = 1 state may be designated as 1($^3\Pi$) as it is a mixture of 90% $^3\Pi$, 5% $^3\Sigma^-$, 3% $^3\Delta$, and 1% $^1\Pi$. Next state with Ω = 1 lies at 31 110 cm^{-1} and it is almost pure $^1\Pi$ state. This is the experimentally known state A1($^1\Pi$). The

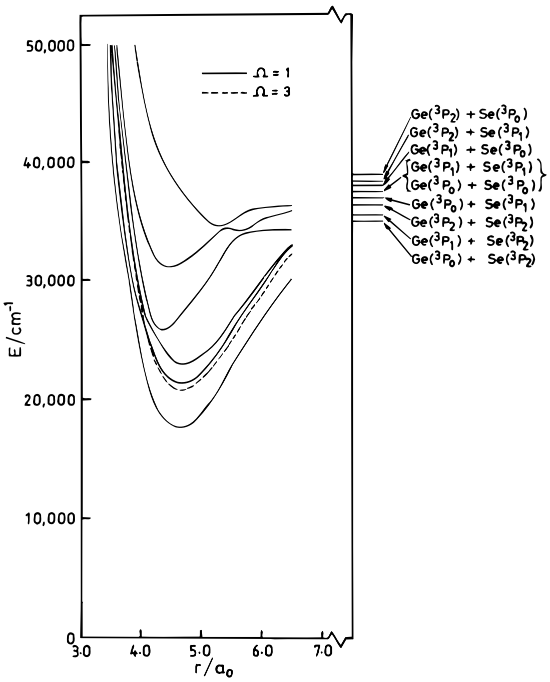

Figure 3. Potential energy curves of low-lying $\Omega = 1$ and 3 states of GeSe.

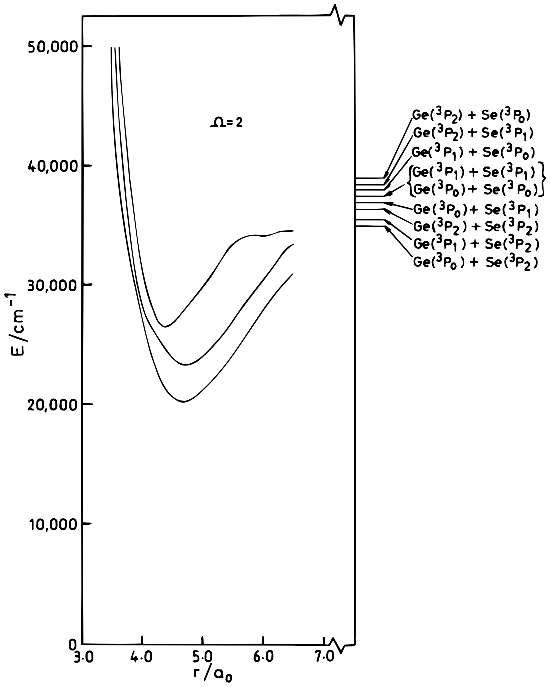

Figure 4. Potential energy curves of low-lying $\Omega = 2$ states of GeSe.

vibrational frequency $\omega_e = 262$ cm^{-1} of this state matches excellently with the experimental value of 269 cm^{-1}.

Transition Probabilities and Lifetimes. There is no experimental data available for the transition probabilities of allowed transitions and lifetimes of the excited states of GeSe. In this study we have calculated the transition probablities of four allowed transitions: $A^1\Pi - X^1\Sigma^+$, $A^1\Pi - {}^1\Delta$, $A^1\Pi - {}^1\Sigma^-$, and $2^1\Sigma^+ - X^1\Sigma^+$. The radiative lifetimes ($v = 0$) of the excited states $A^1\Pi$ and $2^1\Sigma^+$ have been estimated from these transition probabilities. Since the spin−orbit effects on these states concerned are not significant, we have considered only Λ−S states. In Figure 5, we have plotted the calculated dipole transition moments only for the A−X system as a function of internuclear distances. The transition moment decreases smoothly and monotonically. The perpendicular transition A−X is the strongest among all. Other two transitions from $A^1\Pi$ are relatively weak mainly due to the lower energy involved in the transition. Table 6 reports the partial and total radiative lifetime of the two excited states $A^1\Pi$ and $2^1\Sigma^+$. The total lifetime of the A state is estimated from the addition of three transition probabilities is 0.42 μs. The potential energy curve of the $2^1\Sigma^+$ state is very shallow. It consists of only three vibrational levels. However, the transition $X^1\Sigma^+ \leftarrow 2^1\Sigma^+$ is relatively strong, and the calculated lifetime of the $2^1\Sigma^+$ state is 0.45 μs.

TABLE 5: Spectroscopic Constants of Spin−Orbit States of GeSe[a]

state	T_e(cm^{-1})	r_e(Å)	ω_e(cm^{-1})	β_e(cm^{-1})
$X0^+(^1\Sigma^+)$	0	2.172 (2.135)	382 (409)	0.093 (0.096)
$1(^3\Sigma^+)$	17 635	2.445	248	0.073
$0^-(^3\Sigma^+)$	17 900	2.442	246	0.074
$2(^3\Delta)$	20 187	2.480	243	0.071
$3(^3\Delta)$	20 695	2.472	243	0.072
$1(^3\Delta)$	21 223	2.477	241	0.071
$0^+(^3\Sigma^-)$	22 570	2.503	223	0.070
$0^-(^1\Sigma^-)$	22 589	2.518	225	0.069
$1(^3\Sigma^-)$	22 901	2.503	226	0.071
$2(^1\Delta)$	23 300	2.500	240	0.070
$0^+(^3\Pi)$	25 265	2.328	349	0.081
$0^-(^3\Pi)$	25 360	2.330	347	0.081
$1(^3\Pi)$	25 795	2.322	352	0.081
$2(^3\Pi)$	26 475	2.321	361	0.081
$A1(^1\Pi)$	31 110 (30 846)	2.384	262 (269)	0.077

[a] Values in parantheses are taken from the experiment [ref 2].

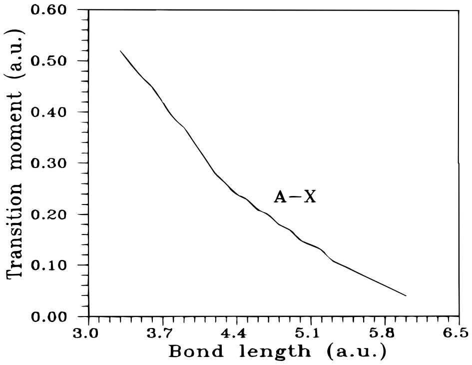

Figure 5. Dipole transition moment of the A−X system of GeSe as a function of bond length.

TABLE 6: Radiative Lifetimes of $A^1\Pi$ and $2^1\Sigma^+$ States of GeSe

transition	partial lifetime of the upper state	total estimated lifetime of the upper state
$X^1\Sigma^+ \leftarrow A^1\Pi$	0.43×10^{-6}	
${}^1\Sigma^- \leftarrow A^1\Pi$	54.7×10^{-6}	
${}^1\Delta \leftarrow A^1\Pi$	56.1×10^{-6}	$\tau(A^1\Pi) = 0.42$ μs
$X^1\Sigma^+ \leftarrow 2^1\Sigma^+$	0.45×10^{-6}	$\tau(2^1\Sigma^+) = 0.45$ μs

IV. Conclusion

There are at least 11 bound Λ−S states of GeSe within 36 000 cm^{-1} of energy as obtained from the MRDCI calculations based on RECPs in which 4s and 4p electrons are kept in the valence shell. Spectroscopic constants of two observed states, namely, the ground ($X^1\Sigma^+$) and the excited ($A^1\Pi$) state agree very well with the calculated values. Spin−orbit effects on the low-lying states are not found to be significantly large. In the present study spectroscopic parameters of the spin−

orbit states are also estimated. The A−X transition is found to be strong. The calculated transition energies and other parameters match excellently with the observed value. One more transition $2^1\Sigma^+-X^1\Sigma^+$ is also considered to be strong. However, the potential energy curve of the excited $2^1\Sigma^+$ state is very shallow. The estimated lifetimes of $A^1\Pi$ and $2^1\Sigma^+$ are around 400 ns.

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