

Static Dipole Moments and Electronic Structure Calculations of the Low-Lying Electronic States of the Molecule Zinc Selenide ZnSe

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Received: May 1, 2017

Accepted: June 11, 2017

Online Published: August 4, 2017

doi:10.5539/mas.v11n9p14

URL: <https://doi.org/10.5539/mas.v11n9p14>

Abstract

Zinc selenide is a compound that has many applications in optoelectrical systems. An understanding of its properties as an individual molecule can be of great help for its use at the nanoscale. Correspondingly, twenty two lowest electronic states of ZnSe have been studied in the $2s+1\Lambda^\pm$ representation in this paper. The potential energy curves, the harmonic frequency ω_e , the electronic energy T_e , the static dipole moment and the internuclear distance r_e have been investigated. These calculations have been performed by using the multi-reference configuration interaction (MRCI+Q) method with Davidson correction. A very good agreement is obtained by comparing the present results with those available in literature. New electronic states have studied in the present work for the first time.

Keywords: *ab initio* calculation, electronic structure, spectroscopic constants, potential energy curves

1. Introduction

Zinc is one of the essential elements for humans by its effects as cofactor for a very large number of enzymes, zinc-finger proteins and matrix metalloproteinases. The calculations of the dipole moment and the bond dissociation of Zn compounds provide critical data for biological simulations and industrial applications (Auld 2001), and (Silva, & Williams 2001). Zinc Chalcogenides have large ionicity of chemical bond with small values of energy for the formation of vacancies. From a stoichiometric ratio of Zn and Se powder, ZnSe molecule can be obtained by microwave irradiation technique (2.8 GHz). These compounds are very promising in optoelectronic applications, i.e in the domains of infrared optics and electro-optic, lenses, laser diodes and electric diodes, beam expanders, semiconductors, and solar cells (Wu, Qiu, Cai, Xu, Chen, & Cryst 2002), and (Porento, & Hirva 2002). The study of the structure and the electronic properties of these compounds at a small scale are needed to understand the applications of these materials. For example, ZnSe nanocluster represents the link between molecules and the bulk of these materials. At the molecular scale, theoretical investigations of the electronic structure of ZnSe are valuable in order to understand their experimentally observed properties. However, no systematic theoretical investigation on the potential energy, the static dipole moment, and the spectroscopic constants of ZnSe molecules have been conducted thus far. In the present work and in order to get further insight into various properties of ZnSe molecule, we extend our investigation to their highly excited electronic states with a rovibrational calculation using the canonical function approach.

2. Method

By using an *ab initio* calculation, we investigate in the present work the low-lying electronic states of ZnSe molecule. The calculation has been performed via CASSCF method. In order to determine the correlation effect, multireference CI calculations were performed using Davidson correction with singly and doubly excitations. In the MRCI calculation, all the CASSCF configuration space has been used as a reference. These calculations have been performed by using the computational chemistry program MOLPRO (MOLPRO 2015) with the graphical user gabedit interface (Allouche 2011). The Zn atom is treated by using the ECP10MDF basis set for the *s*, *p*, and *d* orbitals while the ECP28MWB basis is used for Se atom for the *s* and *p* orbitals; the *d* orbital for this atom is added from the aug-cc-PVDZ;C basis. Among the 24 electrons explicitly considered for the molecule ZnSe, 4 electrons were frozen in our calculation so that 9 valence electrons were explicitly treated. Around the equilibrium position, the molecule ZnSe can be considered ionic as many other transition metals.

3. Results

3.1 Potential Energy Curves and Spectroscopic Constants

In the representation $2s+1\Lambda^{(+-)}$, the calculation of the eleven singlet and eleven triplet potential energy curves (PECs) of the ZnSe molecule has been performed up to 96 internuclear distances in the range of $1.49 \text{ \AA} < r < 4.5 \text{ \AA}$. These curves for the electronic states $^1,^3\Sigma^\pm$, $^1,^3\Pi$, and $^1,^3\Delta$ in the considered range of R are given respectively in Figures 1-5. One can notice that some avoided crossings have been obtained between the potential energy curves $(2)^1\Sigma^+/(3)^1\Sigma^+$, $(1)^1\Pi/(2)^1\Pi$, $(2)^1\Pi/(3)^1\Pi$, $(3)^1\Pi/(4)^1\Pi$, $(2)^3\Pi/(3)^3\Pi$ and $(4)^3\Pi/(5)^3\Pi$. At these avoided crossing the corresponding wave functions will mix with each other to give two adiabatic solutions. These solutions of the Schrödinger equation are obtained by linear combinations of the diabatic ones where the variation method is used. Such crossings or avoided crossings can dramatically alter the stability of the molecule. Because crossing or avoided crossing is near the minima of some of the investigating potential energy curves, the spectroscopic constants for these curves have not been calculated.

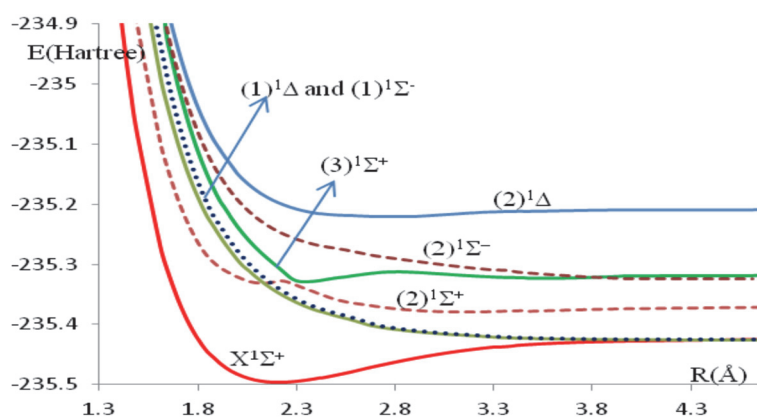


Figure 1. Potential Energy Curves of the Singlet $^1\Sigma^\pm$ and $^1\Delta$ Electronic States of the Molecule ZnSe

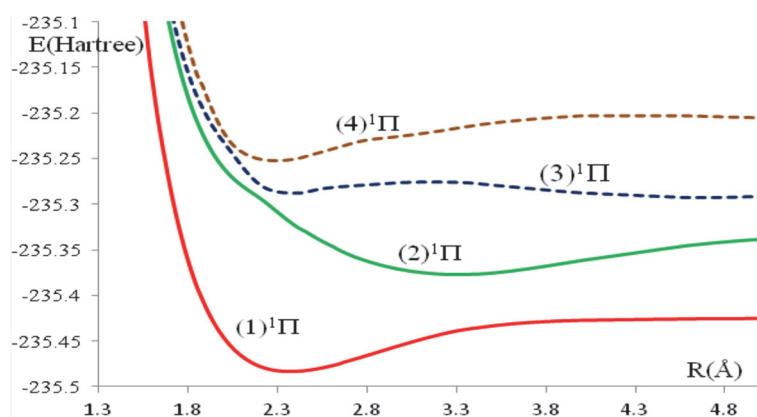


Figure 2. Potential Energy Curves of the Singlet $^1\Pi$ Electronic States of the Molecule ZnSe.

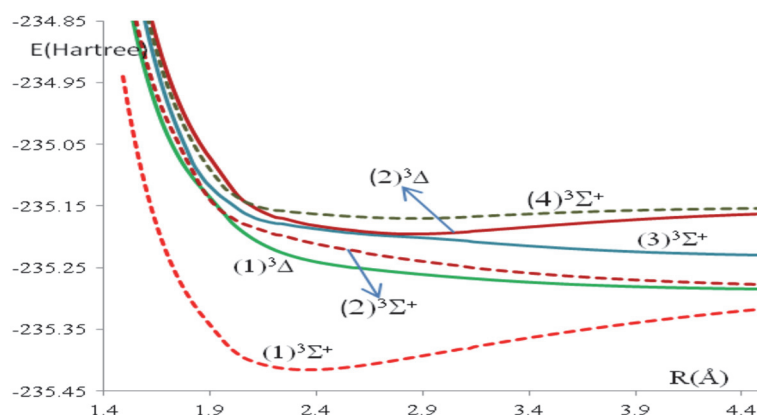


Figure 3. Potential Energy Curves of the Triplet $^3\Sigma^+$ and $^3\Delta$ Electronic States of the Molecule ZnSe

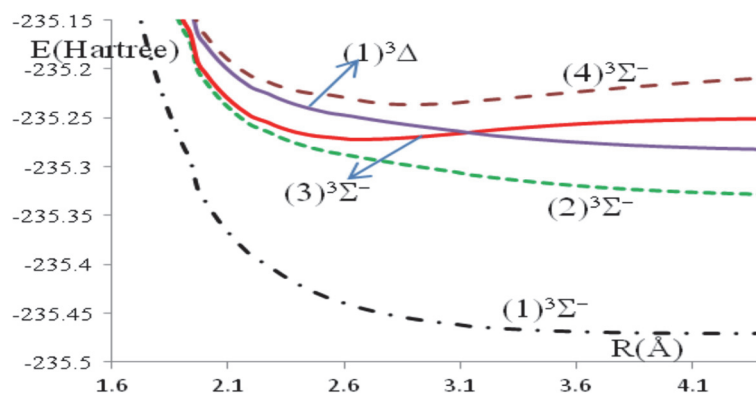


Figure 4. Potential Energy Curves of the Triplet $^3\Sigma^-$ and $^3\Delta$ Electronic States of the Molecule ZnSe

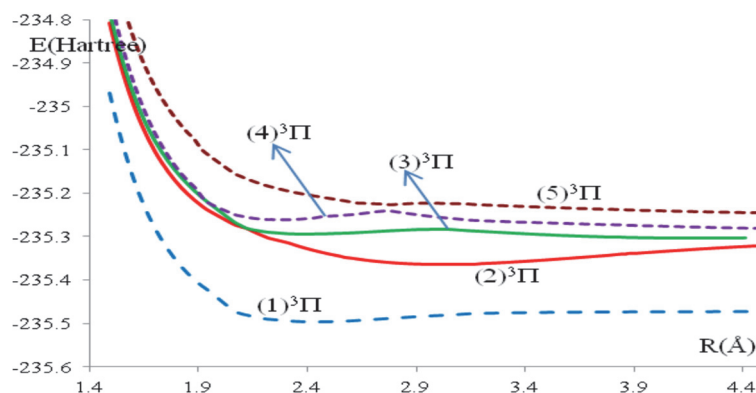


Figure 5. Potential Energy Curves of the Triplet $^3\Pi$ Electronic States of the Molecule ZnSe

For each investigated electronic state, the relative energy with respect to the ground state T_e , the harmonic frequencies ω_e , the rotational constants B_e , and the internuclear distance at equilibrium R_e for the singlet and triplet electronic states of the ZnSe molecule have been calculated by fitting the calculated energy values of the different investigated electronic states into a polynomial in R around the equilibrium values R_e . These values along with those found in literature, either theoretical or experimental, are given in Table 1.

Table 1. Spectroscopic Constants of the Zinc Selenum Molecule ZnSe

States	T_e (cm^{-1})	ω_e (cm^{-1})	B_e (cm^{-1})	R_e (Å)
$X^1\Sigma^+$	0.0 ^a	298.6	0.0965	2.2085
	0.0 ^{b1}	328.9		2.1752
	0.0 ^{b2}	238.5		2.1738
	0.0 ^{b3}			2.163
$(1)^1\Pi$	2900.04 ^a	252.1	0.084	4.475
$(1)^3\Pi$	3536.2 ^a	398.88	0.283	2.436
	3315.7 ^{b3}	238.5		2.353
$(1)^3\Sigma^-$	17674.8 ^a	799.94	0.286	4.577
$(2)^1\Sigma^+$	25726.5 ^a	-	0.051	5.748
$(2)^1\Pi$	26103.4 ^a	136.2	0.043	6.254
$(2)^3\Pi$	28875.2 ^a	277.61	0.181	5.745
$(3)^1\Pi$	45666.0 ^a	306.73	0.083	5.058
$(3)^3\Sigma^-$	49221.0 ^a	322.6	0.234	4.293
$(4)^3\Pi$	51782.5 ^a	322.6	0.091	4.293
$(4)^1\Pi$	53555.8 ^a	286.5	0.089	4.330
$(2)^1\Sigma^-$	58147.7 ^a	383.1	0.055	5.520

^aPresent Work, ^{b1}(Peterson, Shepler, & Singleton-CCSD(T)), ^{b2} (Peterson, Shepler, & Singleton -MRCI+Q), ^{b3}(Peterson, Shepler, & Singleton - using frozen-core MRCI+Q/CBS)

The comparison of our calculated value of the internuclear distance R_e with those given in literature for the ground state (Peterson, Shepler, & Singleton 2007) showed a very good agreement with the average relative difference $\Delta R_e/R_e=1.5\%$; this relative difference becomes 3.4% for the first excited electronic state $(1)^3\Pi$. In literature, there are only 2 theoretical published values for the harmonic vibrational frequency ω_e for the ground state where the difference between them is 90.4 cm^{-1} (Peterson, Shepler, & Singleton 2007). Our calculated value for this constant is closer to that given by (Peterson, Shepler, & Singleton-CCSD(T) 2007), with the relative difference $\Delta\omega_e/\omega_e=9.1\%$ while it is in disagreement with the value given by (Peterson, Shepler, & Singleton -MRCI+Q 2007), where the relative difference is 25.2%. Our calculated value of these constants for the first excited state is smaller than that given by (Peterson, Shepler, & Singleton 2007). There is no comparison of our calculated values of the spectroscopic constants with other data in literature since they are given here for the first time.

3.2 Static Dipole Moment

The vibrational excitation of a molecule depends on the variation of the dipole moment in terms of the internuclear distance. These static dipole moment curves can help in the transition intensities. By taking the atom Zn at the origin, we plot in Figures 6-7 the static dipole moment curves versus the internuclear R for singlet and triplet electronic states of the molecule ZnSe.

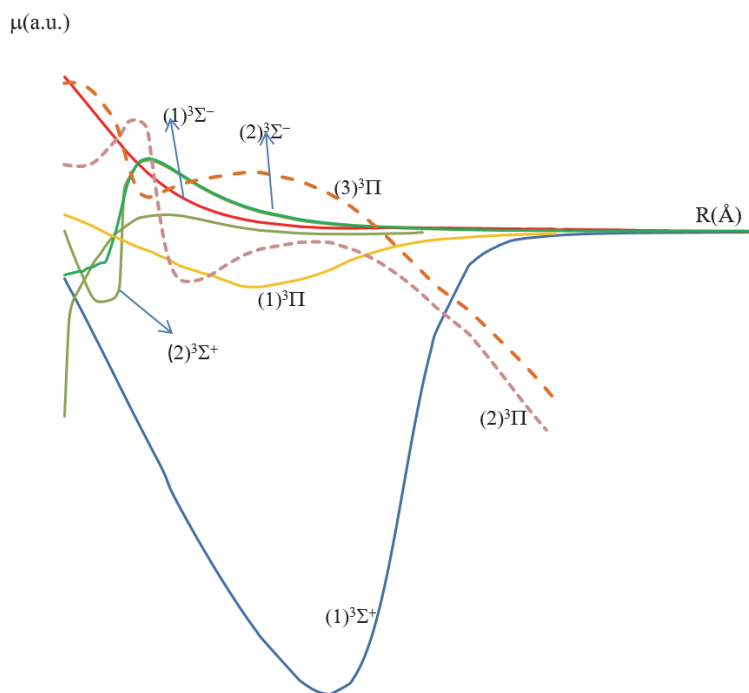


Figure 6. Static Dipole Moment Curves of Triplet Electronic States of the Molecule ZnSe.

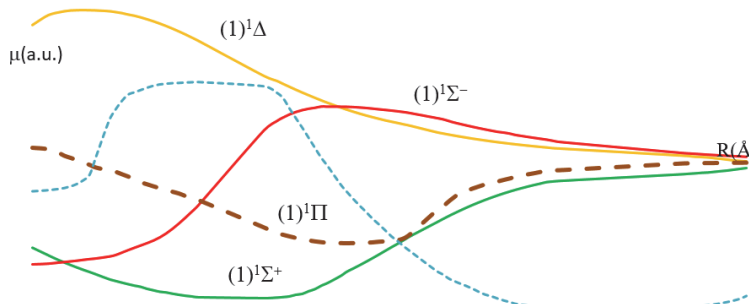


Figure 7. Static Dipole Moment Curves of Singlet Electronic States of the Molecule ZnSe

At large value of the internuclear distances R , the dipole moment curves of the molecule $ZnSe$ tend to approach constant value or zero smoothly where the molecule dissociates into its natural fragments. The advancement in the study of cold and ultracold molecules offers new techniques for precision tests of fundamental physics theories. The vibrational intervals in diatomic molecules are of interest in the context of such an enhancement. Within the Born-Oppenheimer approximation, the radial Schrödinger equation can be replaced, by using the canonical functions approach (Kobeissi, Korek, & Dagher 1989), and (Korek 1999) where the eigenvalues E_v , the rotational constants B_v , and the centrifugal distortion constants D_v have been calculated for the electronic state $(1)^1\Sigma^+$. These values are given in Table 2.

Table 2. The Eigenvalue E_v , the Rotational Constant B_v and the Centrifugal Distortion Constant D_v of the Molecule $ZnSe$

V	E_v (cm ⁻¹)	$B_v \times 10^2$ (cm ⁻¹)	$D_v \times 10^2$ (cm ⁻¹)
0	134.9	9.415	4.897
1	394.8	9.354	4.305
2	661.5	9.344	4.573
3	926.7	9.263	4.915
4	1187.8	9.254	4.091
5	1450.6	9.177	5.075
6	1709.3	9.172	3.654
7	1971.1	9.123	3.958
8	2234.1	9.140	3.229
9	2500.8	9.095	4.862
10	2763.6	9.032	6.475
11	3017.6	8.939	4.461
12	3269.7	8.930	3.677
13	3523.0	8.849	4.946
14	3773.1	8.823	5.433
15	4019.5	8.791	3.839
16	4265.7	8.746	5.028
17	4509.2	8.695	4.954
18	4750.3	8.654	4.364
19	4990.0	8.605	5.089
20	5227.2	8.561	4.743
21	5462.4	8.512	4.790
22	5695.5	8.465	5.019
23	5926.4	8.419	4.868
24	6155.1	8.368	4.896
25	6381.8	8.321	5.125
26	6606.2	8.272	4.968
27	6828.4	8.221	5.063
28	7048.3	8.172	5.256
29	7265.9	8.122	5.150
30	7481.2	8.069	5.233
31	7694.2	8.018	5.464
32	7904.8	7.966	5.409
33	8112.9	7.911	5.439
34	8318.6	7.858	5.635
35	8521.9	7.806	5.580
36	8722.7	7.754	5.409
37	8921.4	7.701	5.651
38	9117.6	7.645	6.348
39	9310.9	7.577	7.027
40	9500.3	7.502	6.931

41	9686.2	7.434	6.596
42	9869.0	7.361	8.511
43	10046.7	7.245	11.62
44	10217.1	7.112	10.39
45	10381.4	7.020	8.005
46	10541.8	6.930	10.35
47	10696.8	6.814	10.54
48	10846.9	6.741	4.158
49	10996.4	6.723	5.630
50	11144.0	6.599	17.62

4. Conclusion

We have presented in this work a precise description of the electronic states of the molecule ZnSe. The data presented can be of great use for scientists and engineers who are interested to work with the compound at the molecular or nanoscale, for both the ground and excited states. Furthermore, based on this study, spin orbital, Einstein coefficient, transitional dipole moments, and Franck-Condon Factor can be performed as future study.

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