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Abstract. The lowest potential energy curves, for the electronic states of the molecule ZnO in the representation $^{2s+1}\Lambda_{(+/-)}$ have been performed via Complete Active Space Self Consistent Field (CASSCF) using the Multireference Configuration Interaction (MRCI) method with Davidson correction (+Q). An excitation and deexcitation model has been proposed, in analogy to the emission of ZnO nanoparticles. In addition, the minimum energy level with respect to the ground state T_e, the internuclear distance at equilibrium R_e, the rotational constant B_e, the vibrational frequency ω_e and the static and transition dipole moment μ have been investigated for some considered electronic states. Ten new electronic states have been investigated here for the first time.

1. Introduction

Metal oxides are characterized by their use in a large versatility of areas, such as enzyme mimetics [1], pharmacology [2-3], fuel additives [4], sensors [5], solar cells [6-8], and antibacterial agents [9]. Zinc Oxide for example, has many applications in optoelectronics and biomedical sciences . Many of these applications rely on the fact that ZnO nanoparticles or quantum dots exhibit quantum confinement effects i.e. their emission properties depend on their size. Mainly the bandgap of such nanometric semi-conductors varies with the size of the nanoparticle. The main objective of this work is to investigate ZnO properties at the smallest possible unit scale, i.e the molecular state. More specifically, we try to understand the electronic structure of the lowest lying electronic states of the metal oxide molecule ZnO. To this end, we performed high level calculations of the electronic structure of ZnO molecule. Ab-initio calculations have been performed via the quantum chemical package MOLPRO [10], taking the advantage of the graphical user GABEDIT [11]. The Zinc atom is treated by using ECP10MDF for s, p, d functions, while the oxygen atom is treated in all electronic scheme by using the AV5Z basis set for s, p, d and f functions. The quality of the selected basis sets is checked by comparing our CI calculations for the ground and several excited electronic states of isolated Zn and O atoms to the experimental data in NIST Atomic Spectra Database. We were additionally interested by the spectroscopic properties of ZnO, and its corresponding dipole moment variation in function of the internuclear distance.

2. Results and discussion

The potential energy curves of ZnO molecule (singlet state) are plotted in figure 1. Singlet states present mostly low energy bound states, with double minima at higher levels ((2)$^1\Pi$, (1)$^1\Delta$).There were no avoided crossings in the studied curves.
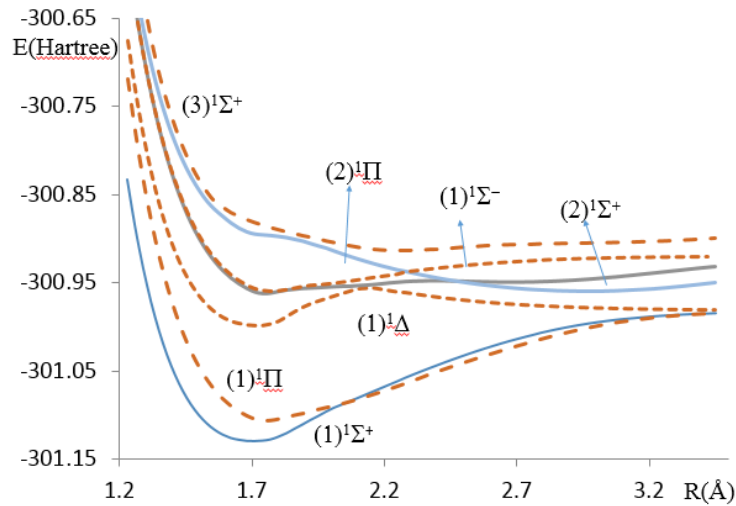
Figure 1. Singlet states potential energy curves.

2.1. Energy levels diagrams

An effective way to represent energy levels of a molecules, and understand possible emission mechanisms is to draw its energy level diagram. In this case one considers the lowest energy value for each potential energy curve, and represents it by a horizontal line. The corresponding Molecular energy level diagram for the molecule ZnO is shown in figure 2.

Figure 2. ZnO energy level diagram.

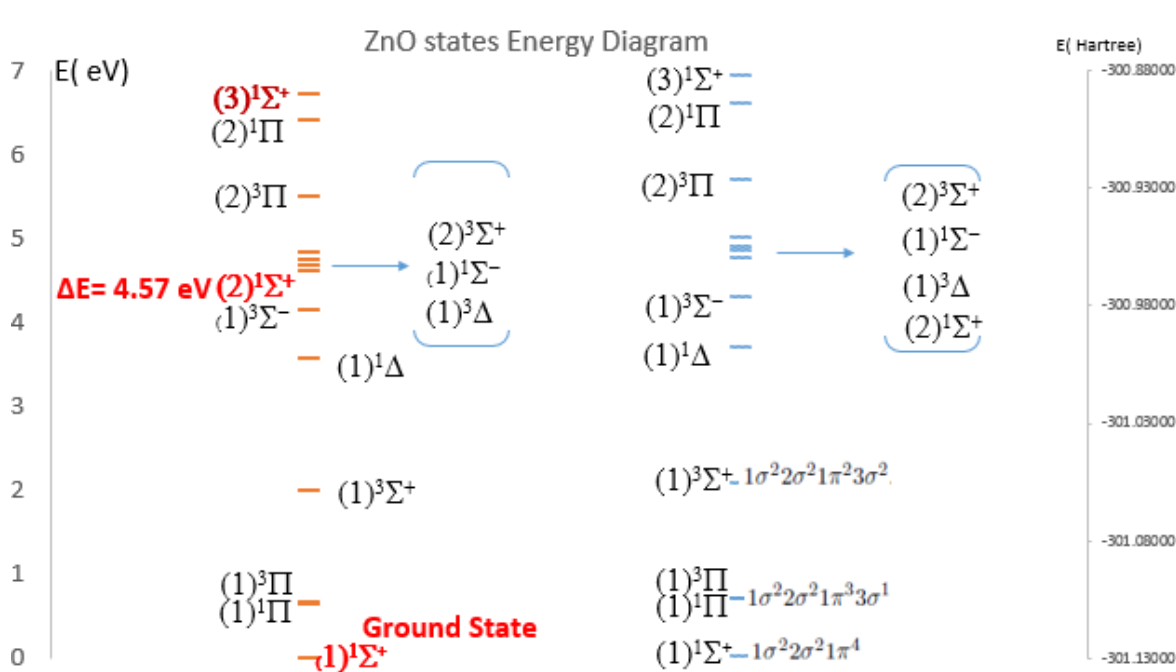ZnO bulk solid is known to emit light with two distinct bands, in UV (~ 3.37 EV) and in the visible part of the spectrum (~2.34 eV) [12]. Quantum dots have been consequently used to understand the origin of the emission bands, in one of the studies for example, the green band was attributed to the excitation of electrons from the conduction band to a deep trap (originating from an oxygen vacancy defect), while the UV emission was attributed to the excitation of electrons from a shallow donor to the valence band [13]. In all cases, ZnO nanoparticles exhibited the behaviour of a band structure whose band gap increased in size, and the nanoparticles got smaller. If one imagines the smallest possible unit of ZnO particles to be the ZnO molecule, then according to the quantum confinement model, its bandgap would be in the orders of 6 eV. In terms of molecular states, the valence band would correspond to a HOMO state while the conduction band, a LUMO one. Up to our knowledge, one experimental study was able to reproduce the emission spectra of ZnO molecules through laser ablation of a ZnO target in vacuum and under oxygen pressure. Even though the spectra were not very clear, ZnO molecular bands were attributed in the green part of the spectrum (between 2.37 eV and 2.18 eV) and violet bands (370-390) were clearly discerned, however they were attributed to ZnO clusters. According to our energy levels diagram, and keeping in mind the molecular states transition rules, an analogy to the band model can be drawn at the molecular level: For the conduction and valence band in nanoparticles corresponds at the molecular level, the HOMO and LUMO levels. The HOMO state would be the electronic ground state $1^1\Sigma^+$, while the LUMO level could be the state $3^1\Sigma^+$. The difference between these two states being equal to about 6.5 eV, as predicted by quantum confinement. Concerning the deep traps, responsible for the green light emission and the shallow donor that caused the violet emission in nanoparticles, their analogous are the allowed states between the HOMO and LUMO states in molecules. More specifically, if an electron is excited to the state $3^1\Sigma^+$ (LUMO level), the energy level diagram and potential energy curves show that its deexcitation to the level $2^1\Sigma^+$ (including the vibrational levels) correspond to an energy of 2.18eV. Thus, the electronic state $2^1\Sigma^+$ plays in this case the role of a deep trap. In other words, this molecular transition would be the analogous of an electron passing from the valence band to a deep drap, as modelled for the green emission in nanoparticles. Similarly, an electron passing from some vibrational level in $2^1\Sigma^+$ to one in the ground state has enough energy to emit light in the violet regime. In this case, the vibrational level would be the shallow donor and the ground state would act as the valence band (or HOMO level).

2.2. *Dipole moment curves*
Dipole moment curves show the variation of the dipole moment with internuclear distance. In this case, we show the dipole moment curves of the singlet states of ZnO molecule.
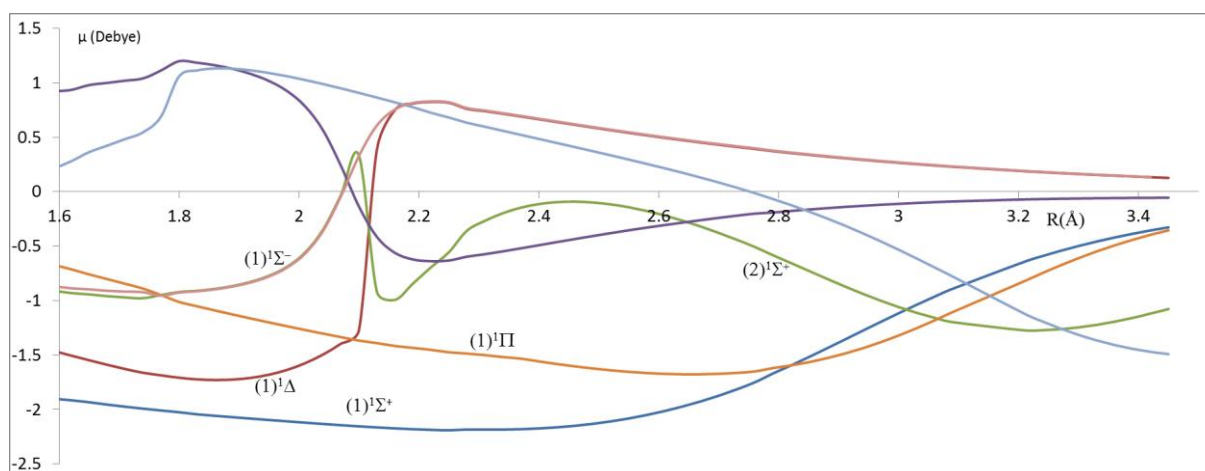

Figure 3. Dipole moment curves of ZnO singlet states.

2.3 Spectroscopic constants

Most of the work found in the literature about ZnO molecules is of theoretical nature, and mainly concerns the two lowest states $(1)^1\Sigma$, and $(1)^3\Pi$. In this paper, we were able to introduce ten additional states. The following table shows the spectroscopic constants of some of the low energy levels of ZnO molecule, in good agreement with previous data in the literature.

Table 1. Spectroscopic constants of ZnO molecule.

State	R_e (a. u.)	T_e (cm^{-1})	B_e (cm^{-1})	ω_e (cm^{-1})	
$(1)^1\Sigma^+$	3.22	0	0.45	770	This work
	3.19	0		766	[15]
	3.24	0		727	[16]
	3.22	0		738	[17]
$(1)^1\Delta$	3.25	28797	0.44	825	
$(2)^1\Sigma^+$	3.305	36897	0.43	1095	
	5.07	39717	0.18	1967	

3. Conclusion

In this paper we have presented a study of the electronic structure of the diatomic molecule ZnO. From the potential energy curves we deduced an energy level diagram that shows the energy difference between the electronic levels. We consequently propose a model that shows an analogy between the molecular and nanometric scales of Zinc Oxide. We have also showed the permanent transition dipole moments and spectroscopic constants of ZnO molecule.

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