

Ab initio configuration interaction study of the ground and low-lying excited states of ZnCd

Feng Gao (高峰), Chuanlu Yang (杨传路), and Yongmian Dong (董永绵)

Department of Physics, Ludong University, Yantai 264025

Received November 7, 2006

The multi-reference configuration interaction (MRCI) electronic energy calculations have been carried out on the ground state ($X^1\Sigma$) as well as three low-lying excited states ($^3\Sigma$, $^1\Pi$, $^3\Pi$) of ZnCd dimer. Potential energy curves (PECs) are therefore generated and fitted to the analytical potential energy functions (APEFs) using the Murrel-Sorbie (MS) potential function. Based on the PECs, the vibrational levels of each state are determined by solving Schrödinger equation of nuclear motion, and corresponding spectroscopic parameters are accurately calculated using the APEFs. The present values of spectroscopic parameters including equilibrium positions and dissociation energies are compared with other theoretical reports available at present.

OCIS codes: 020.0020, 300.6390, 300.6360, 300.6210.

Advances in laser techniques have made the generation of small clusters feasible^[1]. Particularly, the group IIB metal dimers have been the subject of several studies, mainly due to their prospective role as vehicles for excimer laser media with emission in the blue and ultraviolet (UV) wavelength regions^[2]. As the precision of molecular orbital methods for calculating the energies and other spectroscopic constants has been enhanced intensively with the advent of modern computers and the parallel programming methods, we can carry out potential energy curves (PECs) of dimers by high-level *ab initio* calculations, and deduce the analytical potential energy functions (APEFs). Based on these, we can determine their spectroscopic parameters and predict the vibrational levels, which will provide us with abundant information to understand them.

Bieroń *et al.* have performed calculations on the equilibrium position and dissociation energy of the ground state of ZnCd dimer using the second-, third-, and fourth-order Moller-Plesset perturbation theories (MP2, MP3, MP4) and quadratic configuration interaction (QCI) methods^[3]. Czuchaj *et al.* have also carried out multi-reference configuration interaction (MRCI) calculations for the dimer with their own basis sets^[4]. However, the $^1\Pi$ state is not involved in their calculations. It is known that the ground state of the group IIB metal-atom excimer is computationally very challenging, because it presents a shallow minimum arising from van der Waals interactions. Besides, the excited states of the ZnCd dimer are also difficult to be treated because of their deep potential wells. It is not always satisfactory to treat these cases with the calculational methods available at present. The calculated results are affected significantly by the basis sets and configuration state functions (CSFs). Fortunately, the MRCI method enables us to choose suitable CSFs to carry out configuration interaction (CI) calculations. We have studied successfully the ground state of HgZn dimer^[5] using this method. In the present paper, we perform MRCI calculations for the ground state and three low-lying excited states of ZnCd dimer. The spectroscopic properties and vibrational levels based on *ab initio* calculation are reported.

The method used in the calculation is MRCI^[6,7]. We have tried most basis sets available at present for atoms Zn and Cd, and only find one that is effective to both the ground and excited states of ZnCd system. It is LANL2DZ, which is an effective-core potential. For the atom Cd, LANL2DZ means the core orbitals $\dots 4s^2 4p^6$ are replaced by the effective potentials, while the others are defined as the valence orbitals, and for the atom Zn, it denotes that the core orbitals $\dots 3s^2 3p^6$ are replaced by the effective potentials, while the others are defined as the valence orbitals. In the present complete active space self-consistent field (CASSCF) MRCI calculations, the total electrons and active electrons of the four states are all 24. It is easy to understand if we note that 18 electrons of Zn and 36 electrons of Cd are frozen when we employ the basis set LANL2DZ. It should be pointed out that the default reference configuration of Molpro^[8] is only one, when the electronic configuration is completely closed shell. So, if we do not define the occupational orbitals, the MRCI will degenerate into CI with singles and doubles (CISD) treat. In order to obtain more accurate calculation results, we increase the reference configurations. One active orbital was added to the A1 symmetry of the molecule when treating the states $^1\Sigma$ and $^3\Sigma$ then their CSFs increased from 1 to 37 and 20, respectively. As to the $^1\Pi$ state, two active orbitals were added to the spatial symmetry of the molecule, one to the A1 symmetry, and the other to the B1 symmetry, as a result, the CSFs increased to 800. It is important to point out that for this state, the PEC could not reach the asymptotic energy when we added only one active orbital, and accordingly, we added another virtual orbital to increase the quality of the results. As to the $^3\Pi$ state, the orbital was added to the B1 symmetry, and the number of CSFs was 22. The purpose of adding active orbitals to increase the number of CSFs is to improve significantly the calculational bond lengths and dissociation energies, and the CPU times increase very much as well.

The *ab initio* calculations of potential energies were performed with the MOLPRO program package. APEFs were fitted using Murrel-Sorbie (MS) potential and least square fitting method, and the spectroscopic parameters

were determined by the relationship between the potential energy function and themselves. Based on the PECs, the vibrational energy levels were determined by solving Schrödinger equation of nuclear motion. These calculations were realized with program Level 7.5^[9]. All the calculations were carried out on our supercomputer Dawning4000A^[10].

Among the functions that proposed to fit APEFs of diatomic molecules, MS potential energy function seems to be the best. It can accurately reproduce interaction potential energies of many neutral and cationic diatomic molecules, and has been used to deduce APEFs for many molecules^[11–18]. The general MS function is^[19]

$$V(\rho) = -D_e \left(1 + \sum_{i=1}^n a_i \rho^i \right) \exp(-a_1 \rho), \quad (1)$$

where $\rho = R - R_e$, R and R_e are the internuclear distance and equilibrium bond length, respectively. D_e is the dissociation energy. The parameters a_i and D_e are determined by fitting. In many cases satisfactory results can be obtained when n equals 3, while sometimes 4 proves to be better, in other cases more terms are needed. We tried a series of fitting works, and found that for this molecule, accurate results can be obtained when n equals 9.

It is significant to point out that R_e is also treated as a fitting parameter in the fitting process. The spectroscopic parameters can be calculated based on the APEFs. First, the force constants can be determined from the parameters of MS potential energy function,

$$f_2 = D_e(a_1^2 - 2a_2), \quad (2)$$

$$f_3 = 6D_e(a_1 a_2 - a_3 - \frac{a_1^3}{3}), \quad (3)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3 - 24a_4), \quad (4)$$

where f_2 , f_3 , and f_4 are quadratic, cubic, and quartic force constants, respectively. And then, the spectroscopic parameters are

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2}, \quad (5)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 \mu c^2}}, \quad (6)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e} \left(\frac{f_3 R_e}{3f_2} + 1 \right), \quad (7)$$

$$\omega_e \chi_e = \frac{B_e}{8} \left[\frac{-f_4 R_e^2}{f_2} + 15 \left(1 + \frac{\omega_e \alpha_e}{6B_e^2} \right)^2 \right], \quad (8)$$

$$D_{\text{rot}} = \frac{4B_e^2}{\omega_e^2}, \quad (9)$$

where μ is the reduced mass of atoms Zn and Cd, and c is the velocity of light in vacuum.

In the process of present MRCI calculations, the starting internuclear distances of the four states are different,

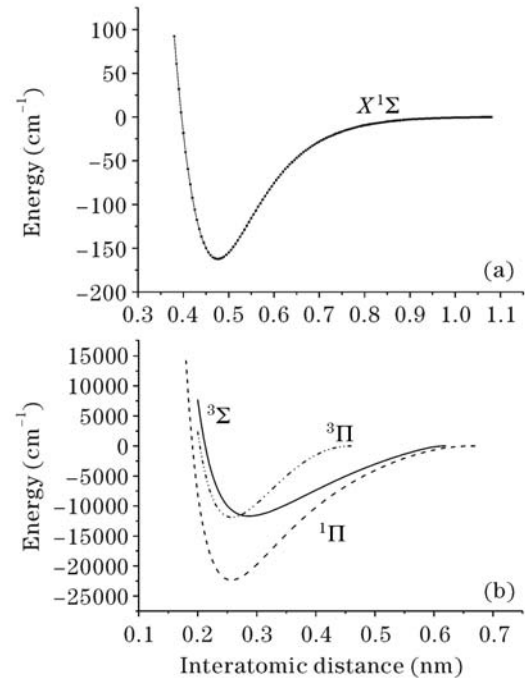


Fig. 1. PECs of the (a) ground and (b) low-lying excited states of ZnCd using MRCI/LANL2DZ calculation.

because their equilibrium positions differ from each other, while 0.005 nm is employed as the step for all the PECs. Figures 1 shows the PECs of the four states. Inspection of the PECs indicates that all the four PECs have reached the asymptotic energy, so we can determine their dissociation energies using the asymptotic energies and the energies at the equilibrium positions. Figure 2 displays intuitively the errors between the fitting PECs and the corresponding *ab initio* ones.

The present results and other theoretical results of equilibrium positions and dissociation energies of the four states are collected in Tables 1 and 2. It is shown in Table 1 that our values of R_e and D_e have obvious discrepancies with the results of Bieroń^[3] and Czuchaj^[4], especially for D_e , which is smaller than all of Bieroń's^[3] results but larger than Czuchaj's value of 125 cm⁻¹. From Table 2 we can see that our D_e of the $^3\Sigma$ and $^3\Pi$ states are also larger than Czuchaj's results. We ascribe the reason to differences of both the calculational methods and the basis sets employed in the calculation. When calculating the ground state $X^1\Sigma$, Bieroń used the MP2, MP3, MP4 and quadratic configuration interaction (QCI) methods and employed a set of basis sets adjusted for the molecules studied by them. However, we can see from Ref. [3] that some of their calculation results of D_e for the ground state of all the group IIB metal dimers except for ZnCd are obviously larger than corresponding experimental values. It is possible that the correlation energies were over-estimated by their calculations. So, it is understandable that our D_e of the ground state of ZnCd is smaller than theirs. Although Czuchaj employed the MRCI method, and their basis sets ($7s7p6d$)/[$6s4p3d$] for Zn and ($8s7p6d$)/[$6s4p3d$] for Cd are relatively larger than our LANL2DZ, their MRCI are simplified according to semiempirical models, and the electronic correlation-energy is not intensively considered, therefore their D_e

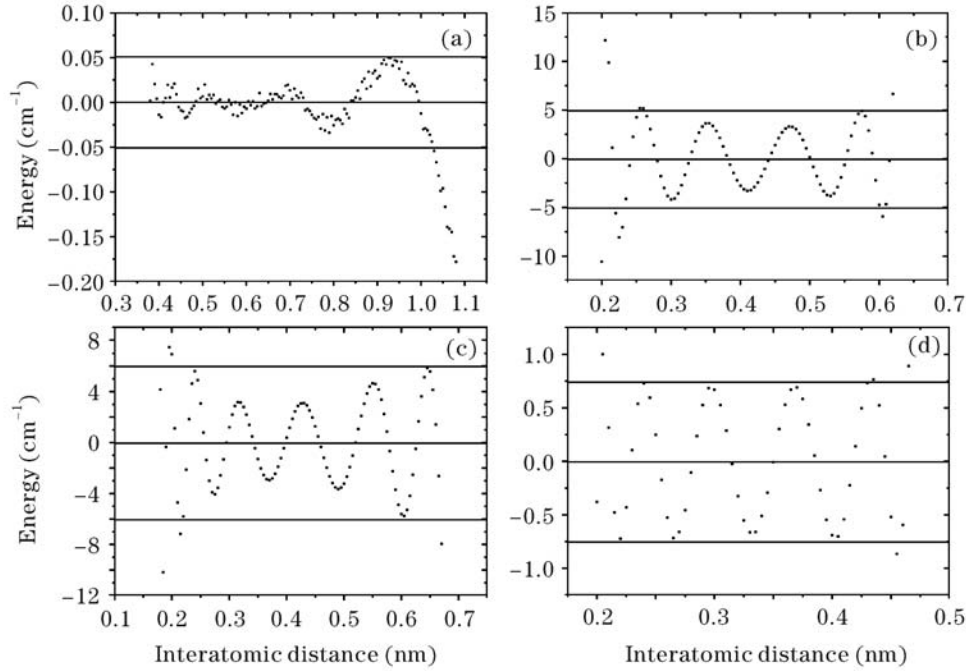


Fig. 2. Fitting errors for the PECs of the (a) $X^1\Sigma$, (b) $^3\Sigma$, (c) $^1\Pi$, and (d) $^3\Pi$ states of ZnCd.

Table 1. Spectroscopic Parameters of the Ground State ($X^1\Sigma$) of ZnCd (cm⁻¹)

	Our Result	Bieron ^[3]				Czuchaj ^[4]
		MP2	MP3	MP4	QCI	
ω_e	15.87					
$\omega_e\chi_e$	0.33					
B_e	0.02					
α_e	3.11×10^{-4}					
$-D_{\text{rot}}$	9.26×10^{-8}					
D_e	162.26	294	237	257	237	125
R_e (nm)	0.476	0.440	0.455	0.450	0.455	0.428

Table 2. Spectroscopic Parameters of the Low-Lying Excited States ($^3\Sigma$, $^1\Pi$, $^3\Pi$) of ZnCd (cm⁻¹)

	Our Result			Czuchaj ^[4]	
	$^3\Sigma$	$^1\Pi$	$^3\Pi$	$^3\Sigma$	$^3\Pi$
ω_e	117.45	189.41	181.74		
$\omega_e\chi_e$	0.33	0.48	0.44		
B_e	0.05	0.06	0.06		
α_e	2.40×10^{-4}	2.23×10^{-4}	2.34×10^{-4}		
$-D_{\text{rot}}$	3.53×10^{-8}	2.64×10^{-8}	2.81×10^{-8}		
D_e	11684.39	22343.40	11888.47	5990	8010
R_e (nm)	0.287	0.257	0.258	0.278	0.259

are smaller than ours. As there is no experimental report on ZnCd, we cannot determine whether our results are better than the other theoretical reports, however, we confirm that our results can give beneficial reference to further investigation of the dimer, especially the $^1\Pi$

state, because there is no research on this state of the ZnCd dimer up to date.

The APEFs are determined by fitting the PECs to the MS potential energy function of Eq. (1). The fitting parameters of MS analytical potential energy function for the states are collected in Table 3. The root means square (RMS) error can be used to evaluate quantitatively the quality of fitting process^[14]. As shown in the table, the smallest RMS is 0.04 cm⁻¹, and even the largest RMS is only 4.05 cm⁻¹, which is much smaller than the chemical accuracy (1.0 kcal/mol or 349.755 cm⁻¹). It proves that our fitting process is of high quality, and MS function is very suitable for reproducing the PECs of the ground and low-lying excited states of ZnCd dimer. Figure 2 shows deviations between the fitting values and *ab initio* data. Although some deviations are relatively large, the percent errors are small. For example, in Fig. 2(b) when R equals 0.2 nm, the deviation is 10.57 cm⁻¹, however, the percent error is only 0.14%. So, we can also conclude that the fitting process is reliable. It is significantly noted that although the dissociation energy of the ground state is very small (only 162.26 cm⁻¹), the MS function remains suitable to reproduce its PECs, because for this state, the largest deviation between the fitting energy and *ab initio* one is only 0.18 cm⁻¹ (when R equals to 1.080 nm), and the value of RMS is only 0.04 cm⁻¹. Tables 1 and 2 list the spectroscopic parameters of the four states, including other theoretical results. There are no more experimental or theoretical reports on the spectroscopic parameters of ZnCd except for R_e and D_e up to date. So, our results can encourage following experimental study on it.

Based on the PECs, the vibrational levels can be determined by solving Schrödinger equation of nuclear motion. Totally, seventeen vibrational levels have been found for

Table 3. Parameters of MS Analytical Potential Energy Function for the Four States of ZnCd

State	$^1\Sigma$	$^3\Sigma$	$^1\Pi$	$^3\Pi$
Range of R (nm)	0.38—1.08	0.20—0.62	0.18—0.67	0.20—0.465
R_e ($\times 10^{-1}$ nm)	4.76	2.87	2.57	2.58
D_e (cm^{-1})	162.26	11684.39	22343.40	11888.47
a_1 ($\times 10$ nm $^{-1}$)	2.65	0.58	1.61	1.59
a_2 ($\times 10^2$ nm $^{-2}$)	2.56	-0.56	0.31	-0.44
a_3 ($\times 10^3$ nm $^{-3}$)	1.29	0.35	0.20	-0.13
a_4 ($\times 10^4$ nm $^{-4}$)	0.45	-0.23	0.03	-0.29
a_5 ($\times 10^5$ nm $^{-5}$)	0.16	0.13	0.06	0.17
a_6 ($\times 10^6$ nm $^{-6}$)	0.05	-0.08	-0.11	-0.12
a_7 ($\times 10^7$ nm $^{-7}$)	0.01	0.03	0.07	-0.02
a_8 ($\times 10^8$ nm $^{-8}$)	0.01	-0.01	-0.02	0.06
a_9 ($\times 10^9$ nm $^{-9}$)	-0.00	0.01	0.00	-0.02
RMS (cm^{-1})	0.04	4.05	3.71	0.60

Table 4. Vibrational Levels of the Four States Based on the Basis Sets LANL2DZ (cm^{-1})

v	$^1\Sigma$	$^3\Sigma$	$^1\Pi$	$^3\Pi$
1	15.20	116.65	188.64	180.93
2	29.72	232.63	376.30	360.97
3	43.54	347.95	562.99	540.12
4	56.63	462.62	748.70	718.38
5	68.97	576.65	933.45	895.75
6	80.55	690.04	1117.23	1072.23
7	91.34	802.81	1300.05	1247.82
8	101.33	914.96	1481.91	1422.50
9	110.50	1026.49	1662.82	1596.29
10	118.82	1137.42	1842.78	1769.17

the ground state $X^1\Sigma$. As the potential well of the excited states are much deeper, there are too many vibrational levels. Only ten vibrational levels for each of the four states are considered in the present paper, and are collected in Table 4. These vibrational energy levels provide the molecular properties for experimental measurement. However, the very narrow gaps of the levels of the ground state imply that they are difficult to observe.

C. Yang is the author to whom the correspondence should be addressed, his e-mail address is yangchuanlu@263.net.

References

- V. E. Bondybed and J. H. English, *J. Chemical Phys.* **74**, 6978 (1981).
- J. Bieroń and W. E. Baylis, *Mole. Phys.* **98**, 1051 (2000).
- J. R. Bieroń and W. E. Baylis, *Chem. Phys.* **197**, 129 (1995).
- E. Czuchaj, F. Rebentrost, H. Stoll, and H. Preuss, *Chem. Phys. Lett.* **212**, 534 (1993).
- F. Gao, C.-L. Yang, and T.-Q. Ren, *J. Mole. Structure (Theochem.)* **758**, 81 (2006).
- H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- P. J. Knowles and H.-J. Werner, *J. Chem. Phys. Lett.* **145**, 514 (1988).
- H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Kauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hample, G. Hetzer, A. W. Loyd, S. J. McNichdas, W. Meyer, M. E. Mura, A. Nicklaß, P. Dalmieri, R. Pitzer, V. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson, *MOL-PRO*, Birmingham University, Cardiff University (2002).
- R. J. Le Roy, *level7.5: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasi-bound Levels* Chemical Physics Research Report No. CP-642R, University of Waterloo (2002).
- Dawning4000A is a large parallel compute containing 134 CPUs (AMD Opteron 64-bit 1.8 GHz) in Ludong University. It is based on Turbo Linux 8.0 and implements with Molpro2002, Gaussian03, Molcas 5.0 and so on.
- C. L. Yang, Z. H. Zhang, and T. Q. Ren, *J. Chem. Phys.* **116**, 6656 (2002).
- C. L. Yang, Z. H. Zhu, R. Wang, and X. Y. Liu, *J. Mole. Structure (Theochem.)* **548**, 47 (2001).
- C. Yang, Z. Zhu, and R. Wang, *Chin. J. Atomic and Molecular Phys.* **18**, 355 (2001).
- C.-L. Yang, Y.-J. Huang, X. Zhang, and K. L. Han, *J. Mole. Structure (Theochem.)* **625**, 289 (2003).
- D. Shi, Y. Liu, J. Sun, Z. Zhu, and X. Yang, *Chin. Opt. Lett.* **3**, 683 (2005).
- C.-L. Yang, X. Zhang, and K.-L. Han, *J. Mole. Structure (Theochem.)* **678**, 183 (2004).
- C.-L. Yang, X. Zhang, and K.-L. Han, *J. Mole. Structure (Theochem.)* **676**, 209 (2004).
- T.-Q. Ren, S.-L. Ding, and C.-L. Yang, *J. Mole. Structure (Theochem.)* **728**, 159 (2005).
- J. N. Murrell and K. S. Sorbe, *J. Chem. Soc. Faraday Trans.* **1552**, 2 (1974).