

# MRCI potential curve and analytical potential energy function of the ground state ( $^1\Sigma^+$ ) of HgZn

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## Abstract

The multireference configuration interaction (MRCI) method is used to calculate a set of energies at different internuclear distances and six different computational levels. Six potential energy curves (PECs) are obtained. Four of them are fitted to analytical potential energy functions (APEFs) using the Murrell-Sorbie potential function, because the dissociation energies and bond lengths of the other ones are obviously not in agreement with the experimental values. Based on the PECs, the vibrational levels are determined by solving Schrödinger equation of nuclear motion, and corresponding spectroscopic parameters are accurately calculated respectively. The values of equilibrium positions and dissociation energies we obtained are compared with other theory and experimental data available at present.

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**Keywords:** Potential energy curve; Analytical potential energy function; Multireference configuration interaction; Spectroscopic parameters; Vibrational levels

## 1. Introduction

Experimental studies of the structure, spectra, and chemical properties of small metal clusters have proliferated recently [1,2]. Advances in laser techniques have made feasible the generation of small clusters [3]. 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 UV wavelength regions [4]. Diatomics such as CdHg and ZnHg have been suggested as likely candidates for high-efficiency laser systems [5]. Despite the ab initio methods for determining properties of atoms and molecules have developed considerably over the last decades, there are still far less theoretical studies on the dimers. As the modern computer techniques develop fast, the computational precision in calculating the molecular energies is increasing rapidly. In the aspect of calculational speed, more and more large parallel computers are used, and the parallel programming methods are enhanced intensively. So, we can carry out high-level ab initio calculations for the PECs of dimers, and induce the APEFs [6]. Based on these, we can determine their spectroscopic parameters and vibrational levels, which will

give information to us to use them widely. In present paper, we will perform systematically this kind of study for HgZn dimer.

## 2. Computational approach

In the calculations, the method we used is the multireference configuration interaction (MRCI) [7,8]. A full CI exactly solves the Schrödinger equation within some basis sets, but is usually too complex a calculation to compute molecules containing more electrons. The single reference methods can almost always be done, and usually are not very challenging (to the computer or the user), however, their accuracy is limited. MRCI is a way to systematically include those CSFs that contribute most significantly to the correlation energy [9]. It is precise in treating small systems, especially dimers. Although there are many basis sets that we can choose, only few ones work well. We have tried many basis sets for atoms Zn and Hg, only four groups of them were seen to give reasonable results. They are (Ahlich-VTZ)Zn/(ECP60MWB)Hg, (ECP10MDF)Zn/(ECP60MWB)Hg, (Ahlich-pVDZ)Zn/(ECP60MWB)Hg and (ECP10MDF)Zn/(ECP78MWB)Hg. It should be noted that M denotes natural atom, DF denotes relativity theory, while WB means quasi-relativity theory. The Ahlich-VTZ is a triple-zeta and full-electron basis set, while Ahlich-pVDZ is also a full-electron basis set, but it is a double-zeta one. ECP60MWB, ECP10MDF and ECP78MWB are all effective-core potentials. Take ECP60MWB for example, for the atom Hg, it means the core orbitals

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...4d<sup>10</sup>4f<sup>14</sup> are replaced by the effective potentials, while the others are defined as the valence orbitals [10]. In the computational process, the numbers of total electrons treated in the above four basis sets are 50, 40, 50, 22, respectively. In the CASSCF/MRCI calculations, number of electrons in valence space is 24 for the anterior three basis sets, and 14 for the last one. So generally speaking, the first and third basis sets are relatively larger, while the last group is the smallest one. Besides, it should be pointed out that although the method we employed is MRCI at first, the default reference configuration of Molpro is only one, because the electronic configuration is completely closed shell. As a result, the MRCI degenerates into CISD treat. In order to obtain more accurate calculation results, we increase the reference configurations. One virtual orbital is added in the A1 symmetry of the molecule in treating the group (ECP10MDF)Zn/(ECP78MWB)Hg, and two virtual orbitals in the active space when using the group (Ahlrichs pVDZ)Zn/(ECP60MWB)Hg (one in the A1 symmetry, the other in the A2 symmetry). Then the corresponding configuration state functions (CSFs) increase to 18 and 865, respectively. The calculational bond length is significantly improved, however, the CPU times increase much as well.

The ab initio calculation of potential energies is performed using the MOLPRO set of program [11]. APEFs are deduced by Murrel-Sorbie potential and least square fitting method, and the spectroscopic parameters are determined by using the relationship between the potential energy function and them. Based on the PECs, the vibrational energy levels were determined by solving Schrödinger equation of nuclear motion. These calculations are realized with program Level 7.5 [12]. All the calculations are carried out on our supercomputer Dawning4000A [13].

### 3. Analytical potential energy function and spectroscopic parameters

Among the functions that proposed to fit APEFs of diatomic molecules, Murrel-Sorbie (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 [14–19]. The general MS function is [20]

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

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 [14–17] when  $n$  equals 3, while sometimes 4 proves to be better [16]. In order to get accurate data, we use the MS function as follow

$$V(\rho) = -D_e (1 + a_1 \rho + a_2 \rho^2 + a_3 \rho^3 + a_4 \rho^4) \exp(-a_1 \rho) \quad (2)$$

It is significant to point out that  $R_e$  is also treated as a fitting parameter during the fitting process. The spectroscopic

parameters can be calculated based on the relationship among spectroscopic parameters and APEF. First, the force constants can be determined from the parameters of MS potential energy function

$$f_2 = D_e (a_1^2 - 2a_2) \quad (3)$$

$$f_3 = 6D_e \left( a_1 a_2 - a_3 - \frac{a_1^3}{3} \right) \quad (4)$$

$$f_4 = D_e (3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3 - 24a_4) \quad (5)$$

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

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2} \quad (6)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 \mu c^2}} \quad (7)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e} \left( \frac{f_3 R_e}{3f_2} + 1 \right) \quad (8)$$

$$\omega_e x_e = \frac{B_e}{8} \left[ \frac{-f_4 R_e^2}{f_2} + 15 \left( 1 + \frac{\omega_e \alpha_e}{6B_e^2} \right)^2 \right] \quad (9)$$

$$D_{\text{rot}} = \frac{4B_e^2}{\omega_e^2} \quad (10)$$

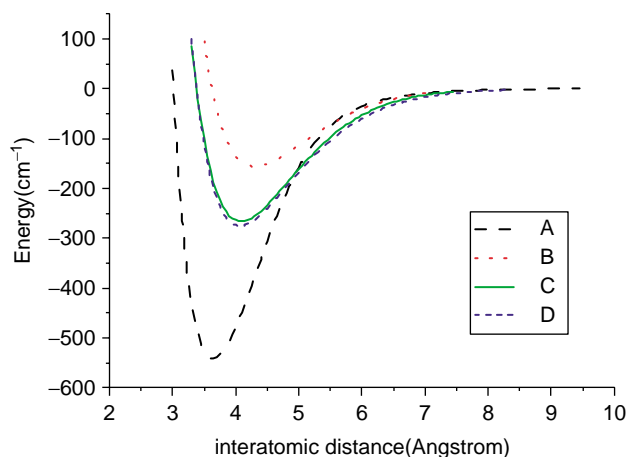
where  $\mu$  is the reduced mass of atoms Hg and Zn, and  $c$  is the speed of light in vacuity.

### 4. Results and discussion

Aiming at increasing the readability, Table 1 lists the basis sets and method for each curve. The calculations at CISD level are started with the internuclear distance of 2.5 Å, and the interval is 0.05 Å. Totally, 140, 95, 100 and 140 points were calculated respectively for each computational level. As for the MRCI calculation, the starting internuclear distance is 3.0 Å, while 0.05 Å is also employed as the interval, and this time 130 points are calculated for both of the two groups. It is known to us all that the properties round the equilibrium position are what we really care, so we just employ 130 in curve A, and 75,

Table 1  
Basis sets and methods for each curve

Curve	Basis sets	Computational method
A	(Ahlrichs-VTZ)Zn/(ECP60MWB)Hg	CISD
B	(ECP10MDF)Zn/(ECP60MWB)Hg	CISD
C	(Ahlrichs-pVDZ)Zn/(ECP60MWB)Hg	CISD
D	(ECP10MDF)Zn/(ECP78MWB)Hg	CISD
E	(ECP10MDF)Zn/(ECP78MWB)Hg	MRCI
F	(Ahlrichs-pVDZ)Zn/(ECP60MWB)Hg	MRCI

Fig. 1. PECs of the ground state ( $1\Sigma^+$ ) of HgZn (CISD).

84,124, 130, 76 points in curve B to curve F, respectively. As we can see, Fig. 1 displays the PECs of each group of basis sets obtained by the CISD method. In Fig. 1, A, B, C, D stand for the four groups of basis sets we have described above. Considering the equilibrium positions and dissociation energy of the system, we can see that only curve C and curve D provide us with relatively reasonable results, and are worthy of further investigation. Neither the equilibrium position nor the dissociation energy in curve A is satisfactory. As to curve B, its equilibrium position is well, but the value of dissociation energy is obviously not in agreement with the experimental counterpart. Fig. 2 shows the two curves obtained by MRCI method, in which E stands for the PEC with the group of basis sets (ECP10MDF)Zn/(ECP78MWB)Hg, and F (Ahlich-pVDZ)Zn/(ECP60MWB)Hg. These two are also used to fit to the MS function, because they also provide us with good results. Although curve E cannot give a satisfactory dissociation energy value, its equilibrium position is better than that of the CISD method. Both the dissociation energy and the equilibrium position in curve F is very close to the experimental data, so it is the best PEC among all of the considered PECs. The least square fitting is a widely used method in fitting work, and in our fitting process, it is realized with the program Origin7.0. Figs. 3–6 display intuitively the

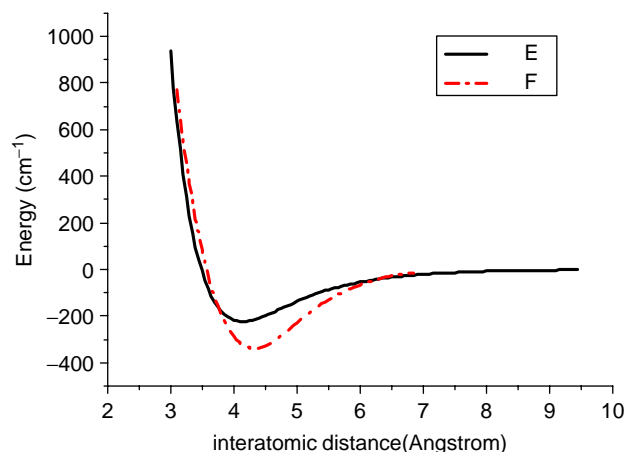
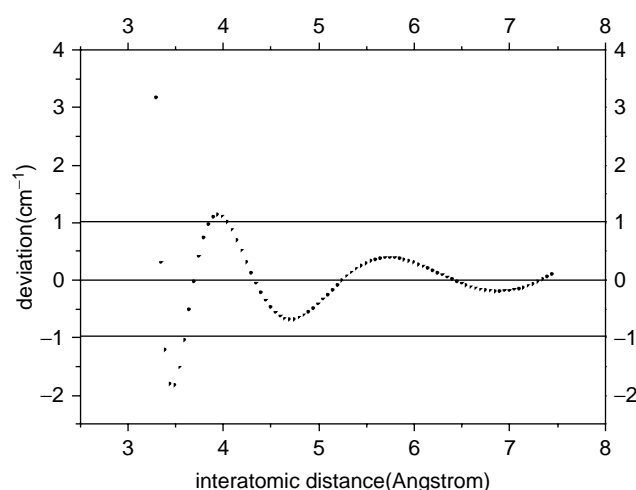
Fig. 2. PECs of the ground state ( $1\Sigma^+$ ) of HgZn (MRCI).

Fig. 3. Fitting error of curve C.

errors between the fitting PECs and the corresponding ab initio ones. The fitting parameters of potential energy function are collected in Table 2. Table 3 shows the spectroscopic parameters of HgZn, while results of other theory as well as the experimental data are also displayed in Table 3. In Table 4 we predict some vibrational levels based on the PECs. The root means square (RMS) error can be used to appreciate quantitatively the quality of fitting process [6]. As is shown in Table 2, the RMS is only 0.68, 3.66, 0.01, and 1.17  $\text{cm}^{-1}$ , respectively, which are much smaller than the chemical accuracy (1.0 kcal/mol or 349.755  $\text{cm}^{-1}$ ). It proves that our fitting process is of high quality, and MS function is very suitable for reproducing the PEC of HgZn dimer. Figs. 3–6 provide deviations between the fitting values and ab initio data. Although some numbers of deviations are large, the percent errors are small. For example, in Fig. 6 at  $R$  equals 3.1 Å, the deviation is 10.28  $\text{cm}^{-1}$ , however, the percent error is only 1.33%. So, we can also conclude that the fitting process is reliable. In Table 3, we can easily see that the spectroscopic parameters obtained by the four levels are in accordance with each other, especially for the values of  $B_e$ . Either the equilibrium bond lengths or the dissociation energies we obtained are close to the experimental data, and our results are better than other works. For example, the best  $D_e$  of our result

Table 2

Parameters of MS analytical potential energy function for the ground state of HgZn

Range of $R/\text{\AA}$	(Ahlich-pVDZ)Zn/ (ECP60MWB)Hg		(ECP10MDF)Zn/ (ECP78MWB)Hg	
	CISD 3.5–7.45	MRCI 3.1–6.85	CISD 3.3–9.45	MRCI 3–9.45
$R_e/\text{\AA}$	4.09	4.32	4.07	4.13
$D_e/\text{cm}^{-1}$	266	333	275	222
$A_1/\text{\AA}^{-1}$	0.9450	1.0470	1.9510	0.9750
$A_2/\text{\AA}^{-2}$	−0.5884	−0.5496	0.8815	−0.7240
$A_3/\text{\AA}^{-3}$	0.0805	−0.1554	0.2117	0.2203
$A_4/\text{\AA}^{-4}$	0.00007	0.07714	−0.01213	−0.02453
RMS/ $\text{cm}^{-1}$	0.68	3.66	0.01	1.05

Table 3  
Spectroscopic parameters of the ground state of HgZn (in  $\text{cm}^{-1}$ )

	(Ahlrichs-pVDZ)Zn/(ECP60MWB)Hg		(ECP10MDF)Zn/(ECP78MWB)Hg		Other theory		Exp[21]
	CISD	MRCI	CISD	MRCI	MRCI [5]	CIS-MP2 [4]	
$\omega_e$	20.5	22.4	20.7	19.1			19.3
$\omega_e X_e$	0.3	0.24	0.1	0.38			0.3
$B_e$	0.02	0.02	0.02	0.02			
$-\alpha_e$	$4.04 \times 10^{-4}$	$1.94 \times 10^{-4}$	$1.81 \times 10^{-4}$	$4.1 \times 10^{-4}$			
$D_{\text{rot}}$	$1.14 \times 10^{-7}$	$0.5 \times 10^{-7}$	$1.16 \times 10^{-7}$	$0.88 \times 10^{-7}$			
$D_e$	266	333	275	223	370	333	310
$R_e/\text{\AA}$	4.09	4.32	4.07	4.13	3.4397 <sup>a</sup>	3.8	4.66

<sup>a</sup> The original value is  $6.50 a_0$ , and is transferred with factor 0.5291772083.

is  $333 \text{ cm}^{-1}$ . It is just a little higher than the experimental value  $310 \text{ cm}^{-1}$ , however, Czuchaj's value is  $370 \text{ cm}^{-1}$ . Our  $\omega_e$  is also in agreement with the experimental value. The  $\alpha_e$  and  $D_{\text{rot}}$  are also calculated, however, no experimental values of them can be used to compare with. It shows that the two basis sets (third and fourth) are better than the others. Furthermore, by a simple comparison, it is safe to say that although we employed the double-zeta and all-electron basis set Ahlrichs-pVDZ for the atom Zn in the CISD calculation, the result is not really better than that of (ECP10MDF)Zn/(ECP78MWB)Hg. It just has a little superiority in computing the equilibrium, but is not so good as the relatively small basis set ECP10MDF in calculating the dissociation energy. However, it is not the same case for the MRCI method, as we can see clearly from Table 3 that the results is much better if we employ basis sets ECP60MWB for Hg and Ahlrichs-pVDZ for the atom Zn. Some contribution is from the aspect of double-zeta and all-electron, and the other is because ECP60MWB is larger than ECP78MWB. Obviously, MRCI is more effective than CISD to

treat present system. It also shows that correlation energy is very important in the PEC of HgZn dimer.

As shown in Table 4, the vibrational energies at four computational levels are also in great agreement to each other. As there is no experimental vibrational levels of HgZn dimer reported up to date, and the experimental spectroscopic parameters are not complete, we are anxious to expect more experimental work to be reported. However, the present results can give reference information to further study.

Table 4  
Vibrational levels with  $J=0$

V	E(v)/ $\text{cm}^{-1}$			
	(Ahlrichs-pVDZ)Zn/ (ECP60MWB)Hg		(ECP10MDF)Zn/ (ECP78MWB)Hg	
	CISD	MRCI	CISD	MRCI
1	18.85	23.92	19.03	18.80
2	37.11	45.86	37.47	36.79
3	54.77	68.12	55.29	53.91
4	71.84	89.13	72.50	70.16
5	88.29	109.63	89.09	85.52
6	104.13	129.52	105.05	99.97
7	119.33	148.29	120.37	113.51
8	133.89	166.55	135.03	126.11
9	147.79	184.03	149.03	137.81
10	161.01	200.46	162.35	148.61
11	173.55	216.19	174.99	158.52
12	185.38	231.17	186.91	167.58
13	196.48	245.23	198.12	175.80
14	206.82	258.37	208.59	183.20
15	216.38	270.69	218.29	189.80
16	225.11	282.17	227.22	195.65
17	232.96	292.78	235.33	
18	239.87	302.40	242.60	
19	245.91	310.74	249.01	

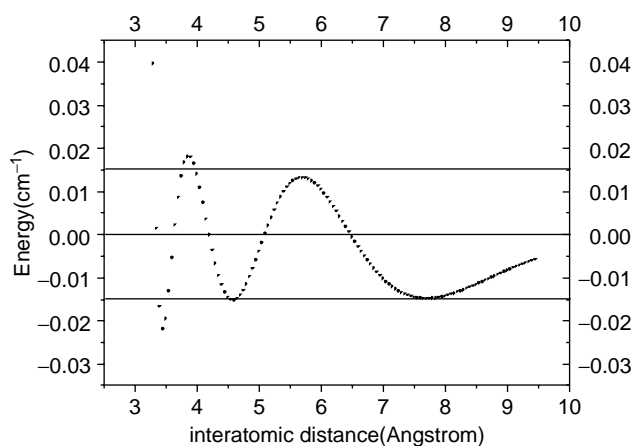


Fig. 4. Fitting error of curve D.

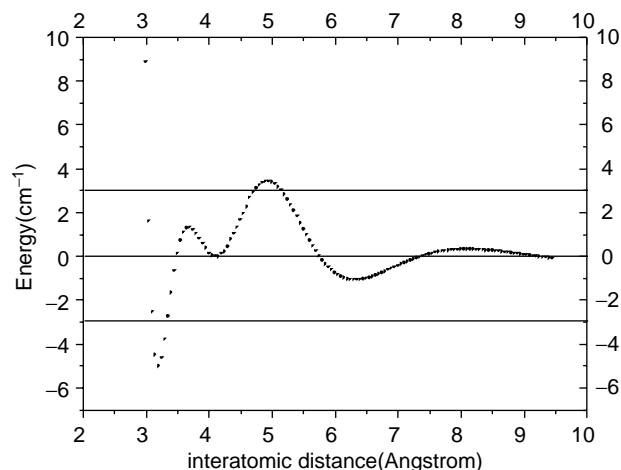


Fig. 5. Fitting error of curve E.

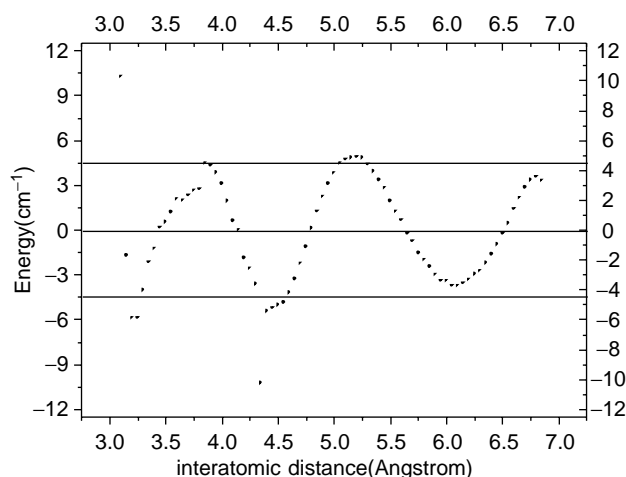


Fig. 6. Fitting error of curve F.

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