[Article]

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含自旋轨道角动量耦合的耦合簇理论研究 Zn_2 和 Cd_2 二聚物的结构和光谱常数

涂喆研^{1,2,*} 王文亮¹⁽¹⁾ 陕西师范大学化学化工学院, 陕西省大分子科学重点实验室, 西安 710062; ⁽²⁾ 西安工程大学理学院, 西安 710048)

摘要: 在二分量相对论有效势和与之匹配的基组 aug-cc-pv n z-pp ($n=Q, 5$) 的基础上, 结合电子相关能的完备基组外推和四阶多项式拟合, 我们用含自旋轨道角动量耦合的耦合簇方法研究了 Zn_2 和 Cd_2 的结构和光谱常数. 尽管 Zn_2 和 Cd_2 的自旋轨道角动量耦合效应不及 Hg_2 的明显, 但还是把自旋轨道角动量耦合放在耦合簇迭代计算中, 以获得更加合理的理论结果. 通过比较, 理论结果与最新发表的实验结果或其他课题组的理论结果吻合得较好, 因此我们的理论计算将有助于丰富对 Zn_2 和 Cd_2 光谱性质的认识.

关键词: 光谱常数; 自旋轨道角动量耦合; 二聚物; 耦合簇方法

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Coupled-Cluster Theoretical Study of Structures and Spectroscopic Constants of Dimers Zn_2 and Cd_2 with Spin-Orbit Coupling

TU Zhe-Yan^{1,2,*} WANG Wen-Liang¹⁽¹⁾ Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China; ⁽²⁾ School of Science, Xi'an Polytechnic University, Xi'an 710048, P. R. China)

Abstract: The structures and spectroscopic constants of Zn_2 and Cd_2 were studied using the coupled-cluster theory with spin-orbit coupling based on the two-component relativistic effective core potential and matched basis sets aug-cc-pv n z-pp ($n=Q, 5$), combining complete basis set extrapolation of the electronic correlation energy and fourth-order polynomial fitting technique. Spin-orbit coupling was included in the post-Hartree-Fock procedure, i.e., in the coupled-cluster iteration, to obtain more reasonable results, although the spin-orbit coupling effect observed in Zn_2 and Cd_2 is not visible as it is in Hg_2 . Our theoretical results agree well with the latest experimental values and other groups' theoretical results, and will be helpful in understanding the spectral characteristics of these two dimers.

Key Words: Spectroscopic constant; Spin-orbit coupling; Dimer; Coupled-cluster theory

1 Introduction

Both relativistic effects and electron correlation are critical to provide reliable theoretical estimates for properties of molecules containing heavy elements.¹ Coupled-cluster theory has been shown to provide an efficient and accurate treatment of electron correlation.² One of the most popular methods nowadays to treat

relativistic effects in an approximate manner is the use of relativistic effective core potentials (ECPs). The interaction of core electrons with the valence electrons is replaced by an effective potential and the core electrons are not longer treated explicitly. Furthermore, when spin-orbit coupling is neglected, it is straightforward to implement scalar relativistic ECPs in the framework of

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*Corresponding author. Email: tuzheyang@126.com; Tel: +86-18392679232.

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non-relativistic calculations since relativity is accounted for only through the parameters of the ECPs. However, spin-orbit coupling has a visible influence on the properties of heavy-element compounds.³ Spin-orbit coupling can also be included using ECPs and such treatments result in two component approaches with the additional advantage that the spin-orbit operator can be represented as a one-electron operator⁴ which can reduce the computational cost very much.

A both efficient and high-precision treatment of spin-orbit coupling based on two component ECPs is to consider the spin-orbit coupling only at coupled cluster level. By including spin-orbit coupling only in the electron correlation part, the Hartree-Fock part and the integral transformation will be exactly the same as in nonrelativistic or scalar relativistic calculations.⁴ It is worthy to mention that coupled cluster theory is able to account for most of the orbital relaxation effects *via* single excitations in the cluster operator.⁵ The advantage of putting the spin-orbit coupling in the post Hartree-Fock part is that the molecular orbitals (MOs) as well as the two-electron integrals in the MO representation remain real and can be classified according to the irreducible representation of the molecular single point group.⁴ This issue can be explored to reduce the computational effort significantly with respect to fully relativistic four component coupled cluster calculations. Therefore, two component ECPs based coupled-cluster theory with spin-orbit coupling is used to study Zn₂ and Cd₂ in this work.

Diatomic molecule formed from two closed shell atoms is van der Waals molecule, Zn₂ and Cd₂ should belong to this category though some authors think that they are not pure van der Waals molecules.^{6–8} The ground states of Zn₂ and Cd₂ are weakly bounded with a large equilibrium distances.

Experimentally, Zn₂ and Cd₂ are less extensively studied than Hg₂ due to their higher vaporization temperatures.^{9,10} Though recent laser spectroscopies of Zn₂ and Cd₂ seem to give reliable values of harmonic frequency (ω_e) and dissociation energy (D_e) of the electronic ground states, the equilibrium distances (R_e) of Zn₂ and Cd₂ are less certain.¹⁰

Theoretically, statement such as “the full consistency with spectroscopic constants coming from experiment has been given up because of the computational demands” appeared in a relativistic calculation paper.¹¹ In recent three years, we find “accurate potential energy curves” calculated with relativistic effects, which considerably narrowed the gaps between theory and experiment,¹² but the discrepancies still remain. It is worthy to mention that Li *et al.*¹⁰ provided the latest theoretical results, but their results relied on potential functional with many parameters.

Most researchers think that the spin-orbit coupling effects of Zn and Cd elements are small^{13–16} and the perturbation method is exact enough to treat the spin-orbit coupling effect of Zn₂ and Cd₂.^{17–19} However, if accurate values of spectroscopic constants are wanted, one would better use iterative method instead of perturbation method to treat spin-orbit coupling. In fact, Kullie has already used a relativistic four-component Dirac-Coulomb Hamiltonian with spin-orbit coupling in the framework of time-

dependent density functional theory and linear response approximation to calculate the electronic state of Zn₂²⁰ and Cd₂.²¹ However, it is widely known that the results of spectroscopic constants are very dependent of the choice of functional. The more general and high-precision *ab initio* calculations are desired and will be helpful to understand the spectral character of these two dimers.

2 Basic equations

The nonrelativistic one-component CCSD (coupled-cluster approach with singles and doubles level) energy equation is then⁴

$$E_{\text{CCSD}} = E_{\text{HF}} + \sum_{i,a} t_i^a f_{ia} + \frac{1}{4} \sum_{i,j} \sum_{a,b} \tau_{ij}^{ab} \langle ij || ab \rangle \quad (1)$$

and the amplitude equations are²²

$$t_i^a D_i^a = f_{ai} + \sum_e t_i^e F_{ae} - \sum_m t_m^a F_{mi} + \sum_{me} t_{im}^{ae} F_{me} - \sum_{nf} t_n^f \langle na || if \rangle - \frac{1}{2} \sum_{mef} t_{im}^{ef} \langle ma || ef \rangle - \frac{1}{2} \sum_{mef} t_{mn}^{ae} \langle nm || ei \rangle \quad (2)$$

$$t_{ij}^{ab} D_{ij}^{ab} = \langle ab || ij \rangle + \mathbf{P}_-(ab) \sum_e t_{ij}^{ae} \left(F_{be} - \frac{1}{2} \sum_m t_m^b F_{me} \right) - \mathbf{P}_-(ij) \sum_m t_{im}^{ab} \left(F_{mj} + \frac{1}{2} \sum_m t_m^e F_{me} \right) + \frac{1}{2} \sum_{mn} \tau_{mn}^{ab} W_{mnij} + \frac{1}{2} \sum_{ef} \tau_{ij}^{ef} \langle ab || ef \rangle - \mathbf{P}_-(ab) \sum_m t_m^b \sum_{ef} \tau_{ij}^{ef} \langle am || ef \rangle + \mathbf{P}_-(ij) \mathbf{P}_-(ab) \sum_{me} (t_{im}^{ae} W_{mbej} - t_i^e t_m^a \langle mb || ej \rangle) + \mathbf{P}_-(ij) \sum_e t_i^e \langle ab || ej \rangle - \mathbf{P}_-(ab) \sum_m t_m^a \langle mb || ij \rangle \quad (3)$$

with the F and W intermediates defined as

$$F_{ae} = (1 - \delta_{ae}) f_{ae} - \frac{1}{2} \sum_m f_{me} t_m^a + \sum_{mf} t_m^f \langle ma || fe \rangle - \frac{1}{2} \sum_{mnf} \tau_{mn}^{ef} \langle mn || ef \rangle \quad (4)$$

$$F_{mi} = (1 - \delta_{mi}) f_{mi} - \frac{1}{2} \sum_e f_{me} t_i^e + \sum_{en} t_n^e \langle mn || ie \rangle + \frac{1}{2} \sum_{nef} \tau_{in}^{ef} \langle mn || ef \rangle \quad (5)$$

$$F_{me} = f_{me} + \sum_{nf} t_n^f \langle mn || ef \rangle \quad (6)$$

$$W_{mnij} = \langle mn || ij \rangle + \mathbf{P}_-(ij) \sum_e t_j^e \langle mn || ie \rangle + \frac{1}{2} \sum_{ef} \tau_{ij}^{ef} \langle mn || ef \rangle \quad (7)$$

$$W_{mbej} = \langle mb || ej \rangle + \sum_f t_j^f \langle mb || ef \rangle - \sum_n t_n^b \langle mn || ej \rangle - \sum_{nf} \left(\frac{1}{2} t_{fn}^{fb} + t_j^f t_n^b \right) \langle mn || ef \rangle \quad (8)$$

the τ amplitudes are defined as

$$\tau_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b - t_i^b t_j^a, \quad \bar{\tau}_{ij}^{ab} = t_{ij}^{ab} + \frac{1}{2} (t_i^a t_j^b - t_i^b t_j^a) \quad (9)$$

the permutation operator $\mathbf{P}_-$ is given by

$$\mathbf{P}_-(pq) f(p, q) = f(p, q) - f(q, p) \quad (10)$$

and the orbital energy denominators are defined as

$$D_i^a = f_{ii} - f_{aa}, \quad D_{ij}^{ab} = f_{ii} + f_{jj} - f_{aa} - f_{bb} \quad (11)$$

The two-component CCSD equations are exactly the same as the above nonrelativistic one component counterparts except that the Fock matrix has contributions from the spin-orbit coupling due to the use of two-component ECPs.

Thus, in the above equations, E_{HF} is the scalar relativistic

Hartree-Fock energy without spin-orbit coupling, $i, j, k, \dots$ are the indices for occupied spin orbitals, $a, b, c, \dots$ denote virtual spin orbitals, and $p, q, r, \dots$ are for general spin orbitals, f_{pq} is the Fock matrix element with the contribution of spin-orbit coupling included. The Fock matrix elements can be written as

$$\begin{aligned} f_{ij} &= \langle i | \mathbf{F}^0 + \mathbf{h}^{\text{SOC}} | j \rangle \\ f_{ab} &= \langle a | \mathbf{F}^0 + \mathbf{h}^{\text{SOC}} | b \rangle \\ f_{ia} &= \langle i | \mathbf{F}^0 + \mathbf{h}^{\text{SOC}} | a \rangle \end{aligned} \quad (12)$$

where $\mathbf{F}^0$ is the Fock operator without spin-orbit coupling and $\mathbf{h}^{\text{SOC}}$ is the spin-orbit coupling operator which is reduced to one-electron operator due to the use of two-component ECPs.⁴

Furthermore, consideration of triple excitations has been shown to be important in order to achieve highly accurate results in coupled cluster calculations.²³ The most popular noniteration scheme to account for triple excitations is the CCSD(T) approach.²⁴ The energy correction due to triple excitation correction is then given by²⁵

$$\Delta E_{\text{T}} = \frac{1}{36} \sum_{ijk} t_{ijk}^{abc} \left[(t_{ijk}^{abc})^* + (\bar{t}_{ijk}^{abc}) \right] D_{ijk}^{abc} + \frac{1}{4} \sum_{ijk} t_{ijk}^{abc} f_{kc}^{ab} (t_{ij}^{ab})^* \quad (13)$$

$$D_{ijk}^{abc} = \mathbf{P}(abc)\mathbf{P}(ijk) \left[\sum_e t_{ij}^{ae} \langle bc || ek \rangle - \sum_m t_{im}^{ab} \langle mc || jk \rangle \right] \quad (14)$$

$$D_{ijk}^{abc} \bar{t}_{ijk}^{abc} = \mathbf{P}(abc)\mathbf{P}(ijk) t_i^a \langle bc || jk \rangle \quad (15)$$

with the cyclic permutation operator

$$\mathbf{P}(pqr)f(p, q, r) = f(p, q, r) + f(q, r, p) + f(r, p, q) \quad (16)$$

It should be pointed out that the occupied-virtual block of the Fock matrix in the second term on the right hand side of Eq.(13) solely comes from spin-orbit coupling. Spin-orbit coupling thus contributes directly to the triple excitation. With respect to the other denominators in Eqs.(1–16), one can find the details in the corresponding literature.

3 Computational details

CFOUR is a program package for performing high-level quantum chemical calculations on atoms and molecules.²⁶ Our coupled cluster calculations in this work are performed in CFOUR package. Both CCSD(T) without spin-orbit coupling and CCSD(T) including spin-orbit coupling (SOC-CCSD(T))²⁷ methods are used to calculate the energies of atoms as well as 9

single point energies of around equilibrium position of these two dimers. The interval of the 9 points is defined to be 0.005 nm. The two-component ECPs, ECP10MDF, and matched basis sets, aug-ccpvnz-pp ($n=Q, 5$)²⁸, are used in the calculations. The electron correlation energies from CCSD(T) and SOC-CCSD(T) are extrapolated to the results of completed basis set (CBS). The formula of CBS for electron correlation energy can be written as

$$\Delta E_{\text{corr}}^n = \Delta E_{\text{corr}}^{\text{CBS}} + \frac{c}{n^3} \quad (17)$$

In the above equation, n is the same to the n in the basis set, the value of n can be defined to be 4, 5 in this work; ΔE_{corr}^n represents the calculated electronic correlation energies from aug-ccpvnz-pp basis sets; the values of c and $\Delta E_{\text{corr}}^{\text{CBS}}$ can be obtained through solving equation sets in Mathematica software package. The Hartree-Fock limit is taken from the aug-ccpvnz-pp basis set. The basis set superposition error (BSSE) is not corrected in this work because of the use of high level basis sets. And the four order polynomial fitting technique is used to calculate the bond lengths and spectroscopic constants of these two dimers and the related fitting formula can be found in the reference²⁹ and references therein.

4 Results and discussion

4.1 Zn₂

The calculated bond lengths and spectroscopic constants, the latest experimental results and other group's theoretical results^{9,10,12} are listed in Table 1. For the bond length, our result from CBS+SOC-CCSD(T) is closest to the result from Pahl *et al.*¹² In Pahl *et al.*'s work, the spin-orbit contribution was obtained from Dirac-Fock calculations and the spin-orbit energies were then added to the scalar energies. For Zn₂ whose spin-orbit coupling effect is weakest, both Pahl *et al.*'s calculated method and our present calculated method are reasonable. With respect to Li *et al.*'s theoretical results, though the optimized potential function is used to determine the structure and spectroscopic constants, the obtained bond length is a bit longer than Pahl *et al.*'s and ours bond length, much shorter than the experimental value.⁹ Perhaps, because of the multi-reference character in Zn₂, both Pahl *et al.*'s and ours *ab initio*'s results are smaller than the experimental value.⁹ In other words,

Table 1 Calculated bond lengths and spectroscopic constants of Zn₂ compared to the latest experimental and other group's theoretical results

	r_e/nm	ω_e/cm^{-1}	D_e/cm^{-1}	$10^2 B_e/\text{cm}^{-1}$	$\omega_e x_e/\text{cm}^{-1}$	$10^4 \alpha_e/\text{cm}^{-1}$
experiment ^a	0.419±0.01	25.90±0.45	242±1		0.69±0.03	
theory ^b	0.3875	25.65	242	3.435	0.709	9.76
theory ^c	0.3826	23.9	223		0.59	9.00
CCSD(T) ^d	0.3853	23.39	236	3.472	1.420	7.48
CCSD(T)+CBS ^e	0.3795	23.35	254	3.580	0.808	5.87
SOC-CCSD(T) ^f	0.3855	23.38	243	3.470	0.317	3.98
SOC-CCSD(T)+CBS ^g	0.3808	25.27	252	3.555	0.482	4.28

r_e : bond length, ω_e : harmonic frequency, D_e : dissociation energy, B_e : rotational constant, $\omega_e x_e$: anharmonicity constant, α_e : vibrational-rotational coupling constant.

^athe latest experimental results, ^bLi *et al.*'s theoretical results, ^cPahl *et al.*'s coupled-cluster calculations with spin-orbit coupling, ^dpresent CCSD(T) method without spin-orbit coupling based on aug-ccpvnz-pp basis set, ^epresent CCSD(T) method without spin-orbit coupling and extrapolate to CBS,

^fpresent SOC-CCSD(T) method based on aug-ccpvnz-pp basis set, ^gpresent SOC-CCSD(T) method and extrapolate to CBS

Table 2 Calculated bond lengths and spectroscopic constants of Cd₂ compared to the latest experimental and other group's theoretical results

	r_e/nm	ω_e/cm^{-1}	D_e/cm^{-1}	$10^2 B_e/\text{cm}^{-1}$	$\omega_e x_e/\text{cm}^{-1}$	$10^4 a_e/\text{cm}^{-1}$
experiment ^a	0.378±0.003	21.4±0.2	328±3		0.35±0.02	
theory ^b	0.4102	21.5	328	1.783	0.367	3.1
theory ^c	0.3847	21.9	340		0.33	3.0
CCSD(T) ^d	0.3855	21.6	347	2.019	0.357	3.7
CCSD(T)+CBS ^e	0.3826	22.8	345	2.049	0.327	3.9
SOC-CCSD(T) ^f	0.3844	23.4	355	2.030	1.597	2.2
SOC-CCSD(T)+CBS ^g	0.3809	23.7	356	2.067	0.622	3.7

^athe latest experimental results,³⁰ ^bLi *et al.*'s theoretical results,¹⁰ ^cPahl *et al.*'s coupled-cluster calculations with spin-orbit coupling,¹²^dpresent CCSD(T) method without spin-orbit coupling based on aug-ccpvtz-pp basis set, ^epresent CCSD(T) method without spin-orbit coupling and extrapolate to CBS,^fpresent SOC-CCSD(T) method based on aug-ccpvtz-pp basis set, ^gpresent SOC-CCSD(T) method and extrapolate to CBS

the noniterative triple excitation in single-reference coupled-cluster procedure may not fully describe the multi-reference character of Zn₂. On the other hand, from our calculated values of bond length, as one can expect, the spin-orbit coupling effect does not change bond length too much, about just 0.001 nm. For other spectroscopic constants in Table 1, all the theoretical results agree with the corresponding experimental results very well. Though the experimental rotational constant and vibrational-rotational coupling constant are absent, all the theoretical values agree with each other very well.

4.2 Cd₂

The calculated bond lengths and spectroscopic constants, the latest experimental results, and other group's theoretical results^{10,12,30} for Cd₂ are listed in Table 2. For the bond length, our result from CBS+SOC-CCSD(T) is closest to the experimental result. The theoretical bond length from Pahl *et al.*'s work is a bit longer than the experimental value. The treatment of spin-orbit coupling in Pahl *et al.*'s work mentioned above may not be the most suitable approach for Cd₂ whose spin-orbit coupling effect is more visible than Zn₂. With respect to Li *et al.*'s theoretical results, though the optimized potential function is used to determine the structure and spectroscopic constants, the obtained bond length is much longer than the experimental value. On the other hand, from our calculated values of bond length, the spin-orbit coupling effect makes the bond length a bit shorter, about 0.002 nm. For other spectroscopic constants in Table 2, all the theoretical results agree with the corresponding experimental results very well. Though the experimental rotational constant and vibrational-rotational coupling constant are absent, all the theoretical values agree with each other very well.

5 Summary

In this work, the two-component coupled-cluster theory with spin-orbit coupling, the completed basis sets extrapolation, and the four-order polynomial fitting technique are used to study the structures and spectroscopic constants of Zn₂ and Cd₂. The results from CBS+SOC-CCSD(T) calculations are the most reliable values in comparison with the latest experimental or other group's theoretical results. The spin-orbit coupling mainly affects the bond

length of Cd₂, and other values are almost not affected by spin-orbit coupling. Our theoretical results will be helpful to understand the spectral character of these two dimers and CBS+SOC-CCSD(T) method is suitable for studying the electronic structures of these van der Waals dimers containing heavy elements.

With respect to Hg₂ whose spin-orbit coupling is most visible, the results of Hg₂ will be reported in the near future due to its complexity.

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