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THEORETICAL INVESTIGATION OF THE SPECTROSCOPIC CONSTANTS OF ALUMINUM CARBIDE IN THE GROUND STATE

X. Liu, L. Li, Z. Qian, X. Wang

School of Mathematics and Physics, Changzhou University, Changzhou, Jiangsu, China
E-mail: xyliu@cczu.edu.cn

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The previous multireference configuration interaction (MRCI) results show that the ground state $^4\Sigma^-$ of the AlC molecule is basically single configurational in nature. In this paper, the potential energy curve (PEC) of $^4\Sigma^-$ is calculated with the Brueckner coupled-cluster doubles with perturbative triple and quadruple corrections [BD(TQ)]. Basis set extrapolations with the correlation-consistent basis sets are performed. The efficiency and precision of the methods with different basis sets are compared. The calculated spectroscopic constants are in excellent agreement with the experimental ones. Our results reveal that the correlation from higher order excitations than doubles is very important for this system.

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Metal carbides represent an important chemical class applied in a wide range of processes and materials. The spectroscopic information of diatomic metal carbide could reveal the aspects of metal-carbon bonding and provide assignments for analytical purposes. The information gained will be the first important step in studying more complex metal carbide systems. Nevertheless, it seems that the basic diatomic species have not attracted wide attention of the scientific community. Until 1990, nothing was known experimentally for the AlC molecule [1]. The very first structure study of AlC was performed by Knight et al. [2], who observed the aluminum carbide (AlC) molecule using matrix isolation electron spin resonance (ESR) spectroscopy. Spin splittings and hyperfine constants were reported and the ground-state symmetry was determined to be $^4\Sigma^-$. C.R. Brazier [3] observed the $B^4\Sigma^-$—$X^4\Sigma^-$ system near 22000 cm^{-1} in the gas phase spectrum of AlC in emission from a composite wall hollow cathode, and estimated the spectroscopic constants of AlC from the emission spectrum. A. Thoma and coworkers measured the binding energy (D_e) of the $X^4\Sigma^-$ state by fluorescence spectrometry in 1993 [4].

As far as the theoretical studies are concerned, the first calculation of the AlC molecule was reported in 1986 by Zaitsevskii et al. [5] using the effective core potential approximation coupled with a limited, perturbatively selected, CI. They identified correctly that the ground state was $X^4\Sigma^-$. Bauschlicher et al. [6] studied the low-lying doublet and quartet electronic states of AlC using the multireference CI methodology. From the calculation they drew the conclusion that $B^4\Sigma^-$—$X^4\Sigma^-$ is the strongest, which was in agreement with the experimental results of Knight et al. [2]. Gutsev et al. [7] determined D_e, the bond length (r_e), and harmonic frequency (ω_e) using the CCSD(T) method. Tzeli and coworkers investigated the ground-state [8] and the excited-state [9] electronic structures using multireference variational methods and large correlation consistent basis sets. Largo et al. [10] and

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Midda et al. [11] calculated the spectroscopic constants of AlC in its ground state using the B3LYP density functional method.

The Level8.0 program can solve the radial or one-dimensional Schrödinger equation for bound and/or quasibound levels of any smooth single or double-minimum potential, and calculate inertial rotation and centrifugal distortion constants, expectation values, and/or Franck—Condon factors and other off-diagonal matrix elements, either for levels of a single potential or between the levels of two different potentials. In this work the spectroscopic constants are calculated with Le Roy′s LEVEL [12] program.

Using a series of increasing size correlation consistent basis sets and the multireference CI approach, we have investigated the ground state of the AlC molecule. We discussed the reasons that make the MRCI method not good for the calculation of spectroscopic constants of the AlC ground state. The deviation must come from the correlation energy. To improve the level of the correlation energy, we used the BD(TQ) method to calculate the spectroscopic constants.

A brief outline of the basis sets and the computational method is given below, further we discuss the results of the calculation, and finally, some conclusions are given.

Basis sets and computational methods. For both Al and C atoms, and the AlC system, the ground state geometry, optimization, and single point energy were calculated at the Brueckner coupled-cluster doubles level with perturbative triples and quadruples [BD(TQ)] [13] using the cc-pVDZ, cc-pVTZ, and cc-PVQZ basis sets respectively. From the optimization and calculation with Level8.0, we get the spectroscopic constants which include the dissociation energy (D_e), the equilibrium internuclear distance (R_e), the harmonic vibrational wavenumber (ω_e), the anharmonicity constant ($\omega_{e,}$ χ_e), and the rotational constant (B_e).

The ground state of the AlC molecule was computed at different levels of theory. The results of multi-configuration methods (such as MRCI, MICR+Q, and CASSCF) compared with the experimental data in Table 1 show that the calculation results of the multi-configuration methods have a large

Table 1

Spectroscopic constants of the AlC *molecule in the* $^4\Sigma^-$ *state: the* BD, BD(T), BD(TQ) *calculation results are obtained at the* cc-pVDZ, *the* cc-pVTZ, *and the* cc-pVQZ *levels. The estimated limit* E_{tot} *is the basis set extrapolations according to Eq*. (2), *and the existing theoretical and experimental spectroscopic constants*

Method		R_e, Å	D_e, eV	ω_e, cm^{-1}	B_e, cm^{-1}	E_{tot}, Hatree
BD	cc-pVDZ	2.0013	2.88	625.7	0.5066	–279.7867669
	cc-pVTZ	1.9758	3.16	647.6	0.5197	–279.8248073
	cc-pVQZ	1.9657	3.28	650.6	0.5271	–279.8350791
	estimated limit	1.9655	3.28	657.8	0.5252	–279.8408243
BD(T)	cc-pVDZ	2.002	3.0	623.2	0.5061	–279.791849
	cc-pVTZ	1.9762	3.28	646.4	0.5195	–279.8325116
	cc-pVQZ	1.9654	3.40	651.2	0.5273	–279.843707
	estimated limit	1.9656	3.40	657.1	0.5251	–279.8496327
BD(TQ)	cc-pVDZ	2.002	3.02	623.8	0.5062	–279.7930223
	cc-pVTZ	1.9761	3.30	646.8	0.5195	–279.8337015
	cc-pVQZ	1.9611	3.41	655.2	0.5277	–279.8447866
	estimated limit	1.9655	3.41	657.4	0.5251	–279.8508296
	Expt. [3]	1.9550		654.84	0.531	
MRCI [6]		1.9781	3.31	629		
MRCI+Q [8]		1.973	3.378	654.2		–279.8465
CASSCF [8]		1.9797	2.96	645.8		–279.717306
DFT/cc-pVTZ [11]		1.976	3.304	622	0.516	
CCSD(T) [7]		1.9544	3.41	658	0.531	–280.014465

deviation from the experimental results. We considered the ground state of AlC to be a single configuration, and when the multi-configuration method is used, we cannot obtain a good result, therefore it is not necessary to use the multi-configuration MRCI method, in which, we guess, the deviation comes from the correlation energy.

The correlation energy is defined as the difference between the energy in the Hartree—Fock limit (E_{HF}) and the exact nonrelativistic energy of a system ε_0

$$E_{\text{corr}} = \varepsilon_0 - E_{\text{HF}}. \tag{1}$$

Also from Table 1 we can see that the results computed with CCSD(T) (including triple excitations non-iteratively) [3] provide rather similar values of the experimental data. However, in [14] it is mentioned that errors in the CCSD(T) atomization energies partially arise from a cancellation of errors resulting from the approximate treatment of the connected triples and from the neglect of the connected quadruple, and that the quadruple correction to the atomization energies is significant and a good estimate is obtained in the cc-pVTZ basis set.

In order to prove that the deviation comes from the correlation energy, we used a series of basis sets with increasing correlation energy, which include the BD, BD(T), and BD(TQ) methods.

Since the correlation-consistent basis sets of Dunning and coworkers [15—17] provide a well-defined series and the calculated energies can be extrapolated to the complete basis set limit [18], in this study we used for extrapolation the data obtained from the correlation-consistent polarized valence double-zeta (cc-pVDZ) and correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis sets. Basis set extrapolations were performed following the work of Halkier et al. [18, 19], and we extrapolated the total energies according to Eq. (2)

$$\Delta E_\infty = \frac{\Delta E_X X^3 - \Delta E_Y Y^3}{X^3 - Y^3}, \tag{2}$$

where X and Y are the cardinal numbers of the basis set, i.e. $X = 2, 3, 4, 5$ for cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z, respectively.

All the theoretical calculations were carried out using the Gaussian-03 program package [20]. The spectroscopic constants are evaluated using Le Roy′s LEVEL program [12].

Results and discussion. The geometric optimization and single point energy calculation of AlC in the $^4\Sigma^-$ state were carried out at the Brueckner coupled-cluster doubles level with BD(TQ) using the cc-pVDZ, cc-pVTZ, and cc-PVQZ basis sets respectively. Then the above calculation results are used as the input for the LEVEL program to assess the effect of basis sets on the spectroscopic constants (including R_e, D_e, ω_e, χ_e, and B_e).

The extrapolation scheme was applied only to energy. Derived spectroscopic constants, such as the bond lengths, harmonic frequencies, and so on, were computed by fitting polynomials to the respective energy points. Spectroscopic constants of the three bound states and the results of estimated basis set limits are summarized in Table 1.

Table 1 lists the data of existing theoretical and experimental spectroscopic constants of AlC in the $^4\Sigma^-$ state.

From Table 1 we can see that the equilibrium bond distance (R_e) decreases on passing from cc-pVDZ to cc-PVQZ; this is in agreement with the theoretical value of Midda et al. [11], and the calculated R_e value is closer to the experimental one, especially the BD(TQ)/cc-pVQZ result with a deviation of only about 0.005 Å.

The harmonic vibrational wavenumber (ω_e) also increases with the improvement of the quality of basis sets; the value is very close to the experimental value of Brazier et al. [3]. Also from Table 1 we obtained that the rotational constant (B_e) values increase with the quality of basis sets; it agrees very well with the experimental value. From Table 1 we found that with the correlation energy increments, the spectroscopic constants are in excellent agreement with the experimental values, and that the extrapolation results are comparable with the cc-PVQZ results. Hence, using this method we can derive spectroscopic constants with the extrapolation equation in the future calculation.

In summary, *ab initio* calculations were carried out for the ground state of the AlC molecule. Potential energy curves (PECs) and spectroscopic constants of $^4\Sigma^-$ states are obtained. We have used a series of increasing quality basis sets, increasing correlation consistent basis sets, and obtained PECs, the equilibrium internuclear distance R_e, the harmonic vibrational wavenumber ω_e, the anharmonicity constant $\omega_e\chi_e$, and the rotational constant B_e. The main findings of this work can be condensed as follows:

1. The ground state of AlC is a single configuration. Multireference configuration interaction (MRCI) calculation results have large deviations compared with the experimental data.
2. With the improvement of the basis sets, the calculated spectroscopic constants are closer to the experimental values.
3. The deviation of the calculated spectroscopic constants comes from the correlation energy. In order to prove this finding, a series of methods with increasing correlation energy was used. Basis set extrapolations with the correlation-consistent basis sets were performed, and we got the spectroscopic constants of the estimated basis set limits. From the comparison we draw the conclusion that the deviation is definitely from the correlation energy.

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