

## КРАТКИЕ СООБЩЕНИЯ

UDC 541.6:546.621:546.17

## POTENTIAL ENERGY CURVES AND CALCULATIONS OF SPECTROSCOPIC CONSTANTS FOR THE GROUND STATE OF AlC AND AlN

X. Liu<sup>1,2</sup>, Y. Yajun<sup>1</sup>, W. Xudong<sup>1</sup>, W. Yehui<sup>1</sup>, J. Meiping<sup>1</sup>, S. Chengxian<sup>1</sup>

<sup>1</sup>School of Mathematics and Physics, Changzhou University, Changzhou, Jiangsu, China,  
e-mail: xianyunliu@gmail.com

<sup>2</sup>Research Center for Advanced Science and Technology, University of Tokyo, Meguro, Tokyo, Japan

Received July, 1, 2011

Revised — September, 21, 2011

The density functional theory method with B3LYP/6-311++G(*df*,*pd*), B3LYP/6-311++G(2*df*, 2*pd*), and B3LYP/6-311++G(3*df*, 3*pd*) basis sets is used to compute the geometrics and single point energy of aluminum carbide (AlC) and aluminium nitride (AlN) in their ground state. The Level 8.0 program is used to calculate spectroscopic constants and fit the energy potential curves. The effect of a basis set on the spectroscopic constants is discussed. The results show that the calculated potential curve matches well with the Level 8.0 fitting curve, and the calculated values of spectroscopic constants become more reliable with the improvement of the quality of basis sets. The spectroscopic constants are in good agreement with the existing experimental and theoretical values. For the first time, the reliable anharmonicity constant data of AlC are reported, which agrees so well with the experimental value.

**Keywords:** spectroscopic constants, potential energy surfaces, level, AlC, AlN.

**Introduction.** Metal diatomic molecules represent an important chemical class that has been applied in a wide range of processes and materials. The information on diatomic molecules is important because of their unique physical, chemical property and applications in catalysis and semiconductor devices. The spectroscopic information about metal diatomics could provide assignments for analytical purposes, and the information gained will be the first important step in studying more complex metal diatomic systems. Nevertheless, it seems that the basic diatomic species have not attracted wider attention of the scientific community. The spectroscopic information on AlC and AlN is still very limited.

Simple diatomic aluminum carbide (AlC) was first observed by Knight *et al.* [1] using matrix isolation electron spin resonance (ESR) spectroscopy. They measured spin splittings and hyperfine constants and determined that the ground-state symmetry was  $^4\Sigma^-$ . This was in agreement with the high-level theoretical calculations of Bauschlicher *et al.* [2]. In their study, Bauschlicher *et al.* studied the low-lying doublet and the quartet of the electronic states of AlC. From the calculation they drew the conclusion that the strongest  $B^4\Sigma^- \rightarrow X^4\Sigma^-$  transition near 22 600  $\text{cm}^{-1}$  is probably the best way to observe AlC in either emission or absorption. Brazier [3] observed the  $B^4\Sigma^- \rightarrow X^4\Sigma^-$  system near 22 000  $\text{cm}^{-1}$  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. Midda *et al.* [4] calculated the spectroscopic constants and molecular properties of AlC in its ground state using a hybrid HF/DF B3LYP method. The theoretical and experimental data on the ground state of AlC are listed in Table 1.

As far as the AlN molecule is concerned, to the best of our knowledge, only one experimental study was performed in 1972 by Simmons and McDonald [5]. They observed AlN emission in the visible region of the spectrum. Based on the rotational analysis of the (0-0) and (0-1) bands, the spec-

Spectroscopic constants of AlC in the  $4\Sigma^-$  state evaluated with Level 8.0

Spectroscopic constants	Basis sets			Other values
	6-311++G(df, pd)	6-311++G(2df, 2pd)	6-311++G(3df, 3pd)	
$R_e$ , Å	1.9746	1.9720	1.9701	1.9550 <sup>a</sup> , 1.9781 <sup>b</sup> , 1.9823 <sup>c</sup>
$D_e$ , eV	3.28797	3.31998	3.32987	3.31 <sup>b</sup>
$\omega_e$ , cm <sup>-1</sup>	625.4198	626.0474	627.1164	654 <sup>a</sup> , 629 <sup>b</sup> , 647 <sup>c</sup>
$\omega_e\chi_e$ , cm <sup>-1</sup>	4.3265	4.2721	4.30244	4.29 <sup>a</sup> , 3.654 <sup>d</sup> , 3.658 <sup>c</sup>
$B_e$ , cm <sup>-1</sup>	0.5205	0.5219	0.52314	0.531 <sup>a</sup> , 0.521 <sup>d,c</sup>

<sup>a</sup> Exp. value, Ref. [ 3 ].

<sup>b</sup> MRCI value, Ref. [ 2 ].

<sup>c</sup> CASSCF value, Ref. [ 2 ].

<sup>d</sup> 6-311++G(2df, 2pd), Ref. [ 4 ].

<sup>e</sup> 6-311++G(3df, 3pd), Ref. [ 4 ].

trum was assigned as a  $3\Pi-3\Pi$  transition. Huber and Herzberg reported the experimental results in their famous book [ 6 ]. The first calculation was performed by Pelissier and Malrieu [ 7 ]; they studied the six lowest states of AlN at the configuration interaction (CI) level, and identified correctly the ground state as  $3\Pi$ . Langhoff *et al.* [ 8 ] studied the low-lying state at the state-averaged complete-active-space self-consistent-field (SA-CASSCF) level and the multireference CI (MRCI) level; they also determined the ground state as  $3\Pi$ . Gutsev *et al.* [ 9 ] and Clouthier *et al.* [ 10 ] also calculated the spectroscopic constants of AlN at CCSD (T) and MRCI levels respectively.

In order to characterize the effect of the basis set on the spectroscopic constants, theoretical calculations were carried out by means of density functional theory (DFT) methods with a series of basis sets. The optimization of the geometry structure and single point energy calculation were made to study the spectroscopic constants and molecular properties of AlC and AlN in their ground state.

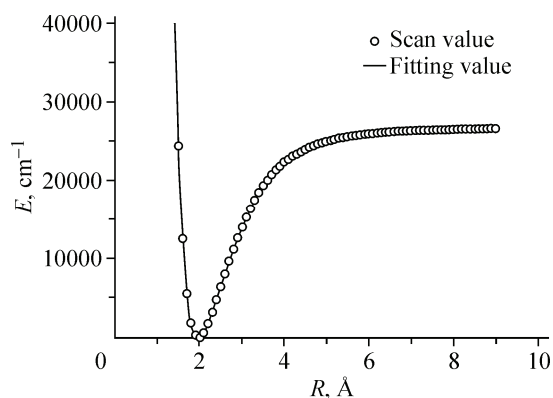
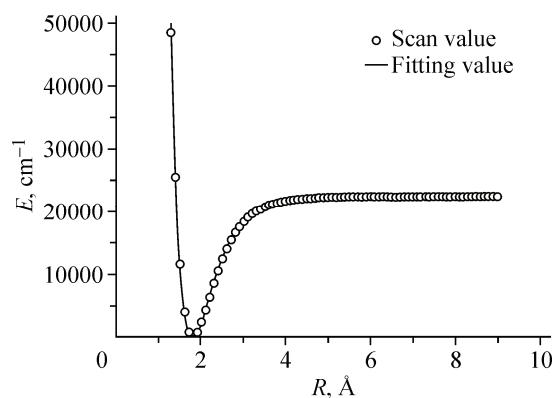
**Computational methods.** The B3LYP [ 11—15 ] method has successfully been applied to study the geometries, frequencies, electron affinities of numerous polyatomic molecule [ 16—18 ] in the past years. In this article, the ground state geometries of AlC and AlN were fully optimized at the DFT level using the B3LYP method; each geometry, optimization, and single point energy were calculated at B3LYP/6-311++G(df, pd), B3LYP/6-311++G(2df, 2pd) and B3LYP/6-311++G(3df, 3pd) levels respectively. From the optimization we get the dissociation energy  $D_e$ . With the dissociation energy and the single point energy scan results as the input file of Level 8.0, the equilibrium internuclear distance  $R_e$ , harmonic vibrational wavenumber  $\omega_e$ , anharmonicity constant  $\omega_e\chi_e$ , and rotational constant  $B_e$  were obtained.

All the theoretical calculations were carried out using the Gaussian-03 program package [ 19 ]. The spectroscopic constants were evaluated using the Le Roy's LEVEL program [ 20 ].

**Results and discussion.** The geometric optimization and single point energy calculation of AlC in the  $4\Sigma^-$  state and AlN in the  $3\Pi$  state were carried out at B3LYP/6-311++G(df, pd), B3LYP/6-311++G(2df, 2pd), and B3LYP/6-311++G(3df, 3pd) levels respectively. The spectroscopic constants were calculated using the Level 8.0 program [ 20 ].

**1. Potential energy curves and spectroscopic constants of AlC.** The potential curve of AlC in the  $4\Sigma^-$  state calculated using the B3LYP/6-311++G(2df, 2pd) basis set and the Level 8.0 fitting curve are plotted in Fig. 1. Fig. 1 shows that the Level 8.0 fitting curve agrees well with the computed potential energy curve.

Then the above B3LYP calculation results are used as the input for the Level 8.0 program [ 20 ] to solve the nuclear Schrödinger equation and to evaluate the spectroscopic constants. The calculated spectroscopic constants (including the equilibrium bond distance  $R_e$ , potential well depth  $D_e$ , harmonic

Fig. 1. Potential energy curves of AlC in the  $4\Sigma^-$  stateFig. 2. Potential energy curves of AlN in the  $3\Pi$  state

vibrational wavenumber  $\omega_e$ , anharmonicity constant  $\omega_e\chi_e$ , and rotational constant  $B_e$ ) of AlC in the  $4\Sigma^-$  state, the existing experimental results [3], and the existing theoretical values [2, 4] are summarized in Table 1. Table 1 shows that the equilibrium bond distance ( $R_e$ ) decreases from 6-311++G(*df*,*pd*) to 6-311++G(3*df*,3*pd*), which is in agreement with the theoretical value of Midda *et al.* [4], and the calculated  $R_e$  value is closer to the experimental value compared with the calculation of Bauschlicher *et al.* [2], with the deviation being only about 0.015 Å.

The dissociation energy ( $D_e$ ) value increases from 6-311++G(*df*,*pd*) to 6-311++G(3*df*,3*pd*) and is very close to the MRCI value in [2]. The harmonic vibrational wavenumber ( $\omega_e$ ) also increases with the improvement of the quality of basis sets, although the value is lower than the experimental value of Brazier *et al.* [3] by about 25  $\text{cm}^{-1}$ . However, it agrees well with the MRCI value [2]. Midda *et al.* [4] calculated the anharmonicity constant ( $\omega_e\chi_e$ ) that has a deviation of 0.6  $\text{cm}^{-1}$  compared with the experimental value, but our  $\omega_e\chi_e$  value agrees well with the experimental value, with a deviation being about 0.01  $\text{cm}^{-1}$ . 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 and the value calculated by Midda *et al.* [4].

**2. Potential energy curves and spectroscopic constants of AlN.** Fig. 2 depicts the potential curve of AlN in the  $3\Pi$  state calculated using the B3LYP/6-311++G(3*df*,3*pd*) basis set and the Level 8.0 fitting curve. From Fig. 2 we can also draw the conclusion that the Level 8.0 fitting curve agrees well with the calculated potential energy curve.

To assess the effect of the basis set on the spectroscopic constants, using Level 8.0 we have calculated the spectroscopic constants (including the equilibrium bond distance ( $R_e$ ), potential well depth ( $D_e$ ), harmonic vibrational wavenumber ( $\omega_e$ ), anharmonicity constant ( $\omega_e\chi_e$ ), and rotational constant ( $B_e$ )) of AlN in the  $3\Pi$  state. A comparison of our values with the experimental data [5, 6] and the results of other high-quality calculations [7–10] are summarized in Table 2. Table 2 shows that all the spectroscopic constants, except for the anharmonicity constant ( $\omega_e\chi_e$ ), are in agreement with the previous results. The equilibrium bond distance ( $R_e$ ) decreases from 6-311++G(*df*,*pd*) to 6-311++G(3*df*,3*pd*) with the improvement of the quality of basis sets; the value is more reliable and in good accordance with the results of the experiment [5, 6] and CCSD(T) calculations [9]. The dissociation energy ( $D_e$ ) value increases from 6-311++G(*df*,*pd*) to 6-311++G(3*df*,3*pd*); the value of the 6-311++G(3*df*,3*pd*) calculation is in excellent agreement with the experimental value [6]. The harmonic vibrational wavenumber ( $\omega_e$ ) also increases with the improvement of the quality of basis sets, and the resulting value is in agreement with the experimental value and the existing theoretical value with a deviation of about 5  $\text{cm}^{-1}$ .

There is no experimental value of the anharmonicity constant ( $\omega_e\chi_e$ ). Our computed values have a large deviation compared with the value obtained by Clouthier *et al.* [10] at the MRCI level, with the deviation being about 1.2  $\text{cm}^{-1}$ . Similarly, the rotational constant ( $B_e$ ) values also increase with the

Spectroscopic constants of AlN in the  $^3\Pi$  state evaluated with Level 8.0

Spectroscopic constants	Basis sets			Other values
	6-311++G(df, pd)	6-311++G(2df, 2pd)	6-311++G(3df, 3pd)	
$R_e, \text{\AA}$	1.7992	1.7941	1.7917	1.7864 <sup>a</sup> , 1.7909 <sup>b</sup> , 1.814 <sup>c</sup> , 1.8082 <sup>d</sup>
$D_e, \text{eV}$	2.7029	2.7565	2.7729	2.78 <sup>a</sup>
$\omega_e, \text{cm}^{-1}$	739.8149	741.4169	742.0313	746.93 <sup>a</sup> , 756 <sup>b</sup> , 746 <sup>c</sup> , 734 <sup>d</sup>
$\omega_e\chi_e, \text{cm}^{-1}$	5.6610	5.6355	5.6394	6.8 <sup>d</sup>
$B_e, \text{cm}^{-1}$	0.5649	0.5680	0.5696	0.5730 <sup>a</sup> , 0.570 <sup>b</sup> , 0.557 <sup>d</sup>

<sup>a</sup> Exp. value, Ref. [ 6 ].

<sup>b</sup> CCSD(T) value, Ref. [ 9 ].

<sup>c</sup> CASSCF value, Ref. [ 8 ].

<sup>d</sup> MRCI value, Ref. [ 10 ].

improvement of the quality of basis sets; it agrees very well with the experimental value [ 5, 6 ] and the results of other high-quality calculations [ 9, 10 ].

**Conclusions.** In summary, *ab initio* calculations by the DFT B3LYP method with 6-311++G(df, pd), 6-311++G(2df, 2pd), and 6-311++G(3df, 3pd) basis sets were carried out for the ground state of AlC and AlN molecules. Potential energy curves and spectroscopic constants of AlC in the  $^4\Sigma^-$  state and AlN in the  $^3\Pi$  state are obtained. The results show that the calculated potential energy curve fitted well with the Level 8.0 fitting curve. As far as the AlC molecule is concerned, to the best of our knowledge, we have obtained reliable  $\omega_e\chi_e$  data and no other theoretical value of the anharmonicity constant  $\omega_e\chi_e$  agrees so well with the experimental value, so it is very useful for future reference. Our computed spectroscopic constants of AlC and AlN in their ground states are all in agreement with the existing values. Judging from the very good agreement with existing, although limited experimental results, and the results of other high-quality calculations, we draw the conclusion that with the improvement of the quality of basis sets, the spectroscopic constants calculated get more reliable.

This work is supported by the Scientific Research Foundation of Changzhou University. The author thanks Dr. Wenli Zou for his useful help and discussion. The authors express gratitude to the referees for their valuable comments.

#### REFERENCES

1. Knight L.B. Jr., Cobranchi S.T., Herlong J.O., Arrington C.A. // J. Chem. Phys. – 1990. – **92**. – P. 5856 – 5866.
2. Bauschlicher C.W., Langhoff S.R., Pettersson G.M. // J. Chem. Phys. – 1988. – **89**. – P. 5747 – 5752.
3. Brazier C. // J. Chem. Phys. – 1993. – **98**. – P. 2790 – 2797.
4. Midda S., Das A.K. // J. Molec. Struct. (Theochem). – 2003. – **633**. – P. 67 – 71.
5. Simmons J.D., McDonald J.K. // J. Mol. Spectrosc. – 1972. – **41**. – P. 584 – 594.
6. Huber K.P., Herzberg G. / Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Co.: New York, 1979.
7. Pelissier M., Malrieu J.P. // J. Mol. Spectrosc. – 1979. – **77**. – P. 322 – 327.
8. Langhoff S.R., Bauschlicher C.W., Pettersson L.G.M. // J. Chem. Phys. – 1988. – **89**. – P. 7354 – 7362.
9. Guisev G.L., Jena P., Bartlett R.J. // J. Chem. Phys. – 1999. – **110**. – P. 2928 – 2935.
10. Clouthier C.M., Grein F., Bruna P.J. // J. Mol. Spectrosc. – 2003. – **219**. – P. 58 – 64.
11. Lee C., Yang W., Parr R.G. // Phys. Rev. B. – 1988. – **37**. – P. 785 – 789.
12. Miehlich B., Savin A., Stoll H., Preuss H. // Chem. Phys. Lett. – 1989. – **157**. – P. 200 – 206.
13. Becke A.D. // J. Chem. Phys. – 1993. – **98**. – P. 5648 – 5652.
14. Stephens P.J., Devlin F.J., Chabalowske C.F., Frisch M.J. // J. Chem. Phys. – 1994. – **98**. – P. 11623 – 11627.

15. *Foresman J.B., Frisch M.J.* / Exploring Chemistry with Electronic Structure Methods, Gaussian Inc., Pittsburgh, 1996.
16. *Boesch S.E., Grafton A.K., Wheeler R.A.* // J. Phys. Chem. – 1996. – **100**. – P. 10083 – 10087.
17. *Boesch S.E., Wheeler R.A.* // J. Phys. Chem. A. – 1997. – **101**. – P. 8351 – 8359.
18. *Raymond K.S., Wheeler R.A.* // J. Comp. Chem. – 1999. – **20**. – P. 207 – 216.
19. *Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A. Jr., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A.* Gaussian 03, Revision B.02, Gaussian, Inc., Pittsburgh PA, 2003.
20. *Le Roy R.J.* LEVEL8.0: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels, Guelph-Waterloo Centre for Graduate Work in Chemistry, Research Report CP-663, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada, 2007; www site <http://leroy.uwaterloo.ca/programs/>.