Vol 18 No 2, February 2009
1674-1056/2009/18(02)/0549-04

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

# The theoretical character of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of ScN*

Bai Feng-Juan(白凤娟), Yang Chuan-Lu(杨传路)†,
Qian Qi(钱 琪), and Zhang Ling(张 玲)

*College of Physics and Electronic Engineering, Ludong University, Yantai* 264025, *China*

(Received 7 April 2008; revised manuscript received 8 September 2008)

This paper calculates the potential energy curves (PECs) of the ground state ($X^1\Sigma^+$) and excited state ($A^1\Sigma^+$) of ScN molecule by multireference configuration interaction method. The correct character of the PECs has been gripped while they had been improperly reported in the literature. Based on the PECs, the spectroscopic parameters and vibrational energy levels are determined, and compared with experimental data and other theoretical works available at the present.

**Keywords:** potential energy curve, spectroscopic parameter, vibrational energy level, multireference configuration interaction

**PACC:** 3150, 3420, 3180

## 1. Introduction

ScN solid is a hard refractory, electrically conducting material,[1] and has widespread use in industry. The ScN molecule is also an interesting subject for researchers in the molecular spectroscopy and molecular structure field, for it is one of the seldom example for which the ground state is formed by the excited states of atoms, i.e., $^4$F state of Sc and the ground state of N. Actually, several scandium compounds ScN and $ScN^+$ have been analysed.[1−3] The experimental study of the $A^1\Sigma^+$ and $X^1\Sigma^+$ state of the ScN molecule is designed by Ram and Bernath[1], which is based on the isoelectronic CaO molecule. Using a Fourier spectrometer, they observed the $A^1\Sigma^+ - X^1\Sigma^+$ system of ScN in emission, and got the equilibrium parameters for the $A^1\Sigma^+$ and $X^1\Sigma^+$. In respect of theoretical investigations, the ground state ($X^1\Sigma^+$) and some lowest excited states have been calculated by Kunze and Harrison[4] using the *ab initio* multiconfiguration self-consistent-field (MCSCF) method. However, there are still gaps between their results and the experiments. Daoudi and Elkhattabi[5] have made better results for the ground state using the configuration interaction by perturbation of a multiconfiguration wavefunction selected iteratively (CIPSI) method. However, their bond length ($R_e$) of $A^1\Sigma^+$ is much shorter than experimental data, and the other molecular parameters of this state are not very well. To make matter worse, the potential energy curves (PECs) of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states are intersected in their results (Fig.1), which should not be intersected according to the avoid intercross rule[6] because the symmetry and the spin of them are completely same. Therefore, more investigations are necessary to understand this molecule correctly. Based on the reliable and high theoretical level *ab initio* multi-reference configuration interaction (MRCI) method and large basis sets, we make a detailed investigation to PECs and spectroscopic properties of the two states ($X^1\Sigma^+$, $A^1\Sigma^+$) of ScN.

## 2. Computational method

The method we used in this study is the internally contracted MRCI, which makes possible to perform considerably high accurate calculations.[7,8] Its wave functions include all single and double excitations relative to complete active space self-consistent field (CASSCF), and yield results which are in close agreement with corresponding uncontracted calculations.[7] Our group has successfully obtained the liable PECs and spectroscopic parameters of many molecules[9−16] with MRCI method.

*Project supported by the National Natural Science Foundation of China (Grant No 10674114).

†Corresponding author. E-mail: yangchuanlu@263.net

For the nitrogen atom, the basis set we used is an augmented triple-zeta (aug-cc-pVTZ). It has a set of 10s, 5p, 2d, and 1f primitive Gaussian functions which are generally contracted to 4s, 3p, 2d, and 1f functions, that is (10s5p2d1f)/[4s3p2d1f].[17] We have tried so many basis sets for atom Sc, but many of them cannot give satisfactory results. Finally, relativistic effective core potentials (RECPs) generated by Dolg and co-workers are employed for Sc. It is called ECP10MDF[12,18,19] which means that the ten electrons of the inner shell ($1s^2 2s^2 2p^6$) are frozen, and the left eleven ones can be active in the configuration interaction space. These active electrons can be described using basis sets as (8s7p6d2f1g)/[6s5p3d2f1g]. So, in the CASSCF/MRCI calculations, the total active electrons of Sc and N reach 18, and the number of active orbitals is 10.

All the calculations of potential energies are performed using the MOLPRO set of programs,[20] and spectroscopic parameters and vibrational levels are calculated in MOLCAS 5.0 program package.[21]

# 3. Results and discussion

## 3.1. The character of the potential energy curves

The PECs of $X^1\Sigma^+$ and $A^1\Sigma^+$ states are obtained through a serial of single energies at MRCI theoretical level. In order to display their character and perform contrasting credibly, both of them are calculated using the same orbitals and shown in Fig.1. 51 energy points are calculated in the range of internuclear distance from 1.18 to 2.18 Å (1 Å=0.1 nm). The PECs of the two states by Daoudi and Elkhattabi using the CIPSI method[5] are displayed in Fig.2.

Just as we well know, the $X^1\Sigma^+$ and $A^1\Sigma^+$ states have the same symmetry and spin, and the curves are impossible to intersect according to the avoid intercross rule,[6] that is, at the same internuclear distance, it is impossible to have the same potential energy for these two states which have the same symmetry and multiplicity. But from the Fig.2, we can see that the two PECs of $X^1\Sigma^+$ and $A^1\Sigma^+$ states intersect each other at about 1.48 Å, which is unreasonable. Fortunately, figure 1 clearly shows that there is no intersection for our PECs for the two states, which indicates that the present calculation has gripped their correct character and the MRCI can give reasonable results for the states of ScN molecule as expected. So, we will investigate more molecular properties for the states based on the present PECs.

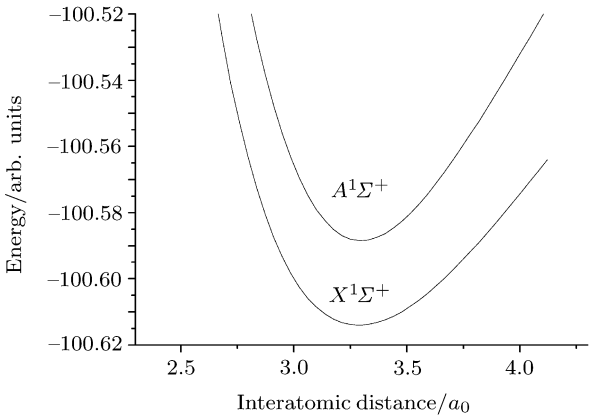



**Fig.1.** The PECs of the two states ($X^1\Sigma^+, A^1\Sigma^+$) of the ScN molecule, computed with MRCI method and aug-cc-PVTZ for N, and ECP10MDF for Sc.

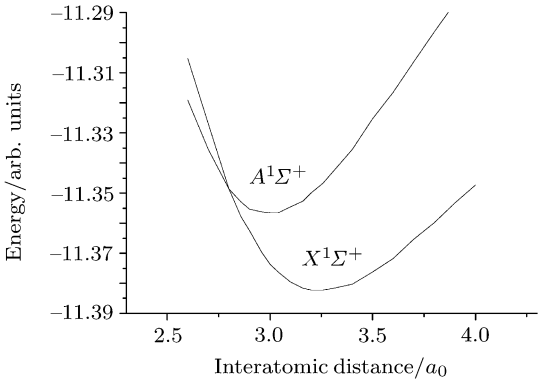



**Fig.2.** The PECs of the two states ($X^1\Sigma^+, A^1\Sigma^+$) of the ScN molecule reported by Daoudi and Elkhattabi.[5]

## 3.2. The spectroscopic properties and vibrational levels

To understand the two states more completely and accurately, we calculate the spectroscopic parameters and vibrational levels of the two states and compare them with experimental data as well as other theoretical results available in the literature. The spectroscopic parameters and vibrational levels are calculated via solving the Schrödinger equation of the nuclear motion. These calculations are realized with MOLCAS program package.[21] All the calculation results are presented in Table 1. In the Table 1, $T_e$ is spectroscopic term and $R_e$ is bond length for the states. $\omega_e$, $\omega_e\chi_e$, $B_e$, $\alpha_e$ and $D_e^c$ represent the harmonic frequency, the anharmonic constant, the rotation constants, the rigid-rotational factor, and the rotation-vibration coupling constant, respectively.

**Table 1.** Spectroscopic parameters for the five states ($X^1\Sigma^+$, $^3\Sigma^+$, $A^1\Sigma^+$, $^1\Pi$, $^3\Pi$) of ScN. $T_e$ in eV, $R_e$ in Å, and other parameters in $cm^{-1}$.

| states | methods | $T_e$ | $R_e$ | $\omega_e$ | $\omega_e\chi_e$ | $B_e$ | $10^{+2}\alpha_e$ | $10^{+5}D_e^c$ |
|---|---|---|---|---|---|---|---|---|
| $X^1\Sigma^+$ | Expt[1] | 0.000 | 1.687 | 795.0 | – | 0.5546 | 0.3718 | 0.1068 |
| | MCSCF[4] | 0.000 | 1.768 | 726.0 | 0.30 | 0.5050 | 0.0300 | 0.0979 |
| | CIPSI[5] | 0.000 | 1.714 | 765.5 | 4.36 | 0.5370 | 0.4184 | 0.1057 |
| | Present | 0.000 | 1.750 | 806.6 | 3.76 | 0.5153 | 0.1153 | 0.0862 |
| $A^1\Sigma^+$ | Expt[1] | 0.706 | 1.695 | 1045.0 | – | 0.5492 | 0.1798 | 0.0608 |
| | CIPSI[5] | 0.707 | 1.584 | 1025.2 | 6.48 | 0.6290 | 0.5118 | 0.0947 |
| | Present | 0.724 | 1.697 | 1063.2 | 7.05 | 0.5478 | 0.3485 | 0.0583 |

As previously mentioned, there are two theoretical investigations about the ground state and some low-lying excited states of the ScN molecule in the literature. One of them is performed with MCSCF,[4] and the other with CIPSI.[5] Let us analyse the ground state at first. From the Table 1, we can see that, for the bond length $R_e$ , the present value 1.75 Å is better than 1.768 Å of Kunze[4] in comparison with the experimental datum 1.687 Å. As for the harmonic vibrational frequency, the present value 806.6 $cm^{-1}$ is obviously better than 726.0 $cm^{-1}$ of Kunze in comparison with the experimental datum 795.0 $cm^{-1}$,[1] while 765.5 $cm^{-1}$ of Daoudi[5] is not so good in comparison with our data and the experiment. We can conclude that both the bond length and the harmonic vibrational frequency are improved in the present calculations. As for the other parameters, ours are more close to the experimental data in comparison with MCSCF method of Kunze although some deviations from the experimental data still exist. It should be noted that the ground state of ScN molecule is composed of the excited state ($^4$F) of Sc atom and the ground state ($^4$S) of N atom, which makes it difficult to treat for general computational method. Therefore it is not surprising that the present computational results still have some deviations from the experimental data although high-level MRCI method and large basis set aug-cc-PVTZ are employed.

Now we take the excited state $A^1\Sigma^+$ into account. The Table 1 shows that the values of $R_e$ and $\omega_e$ of $A^1\Sigma^+$ are 1.697 Å and 1063.2 $cm^{-1}$, respectively, and the deviations between our data and the experimental values are 0.118% and 1.74%, respectively. We can compare our results of the state with those of Daoudi, since Kunze has not treated this state in their MCSCF calculations. Using the CIPSI method, Daoudi provided the corresponding values which are 1.584 Å and 1025.2 $cm^{-1}$. The errors between them and the experimental data are 6.55% and 1.89%, respectively. Obviously, our results are significantly improved in comparison with those of Daoudi. One can also find from the Table 1 that the other spectroscopic parameters are much better than the CIPSI in comparison with experimental data. On the whole, the results for $A^1\Sigma^+$ are better than those of the $X^1\Sigma^+$ state as discussed above in comparison with the experimental data and theoretical results in the literature.

In order to further study the properties of the two states, we calculate the vibrational energy levels of these two states using the obtained PECs. They are presented in Table 2. $E_1$ and $E_A$ are the energy levels of the $X^1\Sigma^+$ and $A^1\Sigma^+$ states, respectively. Unfortunately, to our best knowledge, there are no experimental energy levels reported for them up to date. Considering that the spectroscopic parameters at present computational level are in good agreement with the experimental values, we believe that these vibrational energy levels based on the same PECs are credible and can be used as a useful guide for future theoretical investigations or experimental measurements.

**Table 2.** Vibrational levels with $J$=0, $E_1$ and $E_A$ in $cm^{-1}$. The vibrational ground state of the electronic excited state is set to zero for convenience.

| $v$ | $E_1$ | $E_A$ |
|---|---|---|
| 0 | 0.00 | 0.00 |
| 1 | 799.69 | 1049.19 |
| 2 | 1591.52 | 2085.32 |
| 3 | 2376.43 | 3107.99 |
| 4 | 3154.92 | 4117.56 |
| 5 | 3927.89 | 5115.10 |
| 6 | 4695.04 | 6100.95 |
| 7 | 5456.48 | 7074.93 |
| 8 | 6212.05 | 8037.77 |
| 9 | 6961.73 | 8989.60 |

# 4. Conclusion

The correct PECs of the two $\Sigma^+$ states of ScN molecule, which have been reported improperly in the literature, have been obtained using the high level MRCI method and large basis sets. Moreover, spectroscopic parameters of them, especially of the excited state $A^1\Sigma^+$, are obviously improved in our calculations in comparison with the experimental data and theoretical results in the literature. However, for some spectroscopic parameters, there are still gaps between the experimental data and the theoretical values. Therefore, more complicated method is still expected to more accurately describe such a particular molecule that the ground state is formed from the excited states of atoms.

# References


[1] Ram R S and Bernath P F 1992 *J. Chem. Phys.* **96** 6344
[2] Jeung G H and Koutecky J 1988 *J. Chem. Phys.* **88** 3747
[3] Kunze K L and Harrison J F 1989 *J. Phys. Chem.* **93** 2983
[4] Kunze Kathryn L and Harrison James F 1990 *J. Am. Chem. Soc.* **112** 3812
[5] Daoudi A, Elkhattabi S and Berthier G 1998 *Chem. Phys.* **230** 31
[6] Gerhard Herzberg 1950 *Molecular Spectra and Molecular Structure* (Canada: Van Nostrand)
[7] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803
[8] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514
[9] Gao F, Yang C L, Hu Z Y and Wang M S 2007 *Chin. Phys.* **16** 3668
[10] Zhang X Y, Yang C L, Gao F and Ren T Q 2007 *Mol. Struct. (THEOCHEM)* **816** 97
[11] Qian Q, Yang C L and Gao F 2007 *Acta Phys. Sin.* **56** 4420 (in Chinese)
[12] Gao F, Yang C L and Zhang X Y 2007 *Acta Phys. Sin.* **56** 2547 (in Chinese)
[13] Yang C L, Zhang X Y, Gao F and Ren T Q 2007 *Mol. Struct. (THEOCHEM)* **807** 147
[14] Zhang X Y, Yang C L, Gao F and Ren T Q 2006 *Chin. Phys.* **15** 1981
[15] Gao F, Yang C L and Ren T Q 2006 *Mol. Struct. (THEOCHEM)* **758** 81
[16] Yang C L, Gao F, Zhang X Y and Han K L 2005 *J. Chem. Phys.* **123** 204308
[17] Kendall R A and Dunning T H 1992 *J. Chem. Phys.* **96** 6796
[18] Dolg M, Wedig U, Stoll H and Preuss H 1987 *J. Chem. Phys.* **86** 866
[19] Stoll H, Metz B and Dolg M 2002 *J. Comput. Chem.* **23** 767
[20] Werner H J, Knowles P J, Lindh R, Manby F R, Schütz M and others 2002 *MOLPRO, Universität Stüttgart* (Stüttgart: Germany) *University of Birmingham* (Birmingham: United Kingdom)
[21] Karlström G, Lindh R, Malmqvist P A, Roos B O, Ryde U, Veryazov V, Widmark P O, Cossi M, Schimmelpfennig B, Neogrady P and Seijo L 2003 *Comp. Mater. Sci.* **28** 222