Vol 17 No 12, December 2008
1674-1056/2008/17(12)/4481-04

Chinese Physics B

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The theoretical study on the potential energy curves for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule*

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(Received 18 March 2008; revised manuscript received 9 June 2008)

This paper applies the symmetry-adapted-cluster/symmetry-adapted-cluster configuration-interaction (SAC/SAC-CI) method to optimize the structures for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule with the basis sets D95++, 6-311++G and 6-311++G**. Comparing the obtained results with the experiments, it gets the conclusion that the basis set 6-311++G** is most suitable for the optimal structure calculations of $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule. The whole potential energy curves for these electronic states are further scanned by using SAC/6-311++G** method for the ground state and SAC-CI/6-311++G** method for the excited states, then use a least square method to fit Murrell–Sorbie functions, at last the spectroscopic constants and force constants are calculated, which are in good agreement with the experimental data.

Keywords: SAC/SAC-CI, SiO, potential energy function, spectroscopic constants
PACC: 3120, 3150, 3620K

1. Introduction

To make the molecular spectroscopic properties understandable thoroughly, it is necessary to set reliable physical models of bonding potentials, since quantitative molecular spectroscopic knowledge can be derived from the molecular analytic potential energy function (APEF).[1] With the development of modern quantum chemical methods and the improvement of computer calculating speed, *ab initio* can give progressively more accurate potential energy curves, especially for the small molecules. It is possible that more comprehensive and reliable results for higher excited electronic states can be obtained. There is a long-standing interest in simple and reliable analytical models of chemical potentials, which consist of physically identifiable terms and are based on a limited number of available theoretical data.

SiO is a kind of extremely good silicon-based luminescent material. Along with the widespread applications in optical coating materials, high-silica glass materials and so on, the study on the properties of silica system becomes the foundational popular topic of this material. The molecular potential energy function is the complete description of the molecular electronic structure[1−6] and the foundation for the study of molecular reaction dynamics. For SiO molecule, the potential energy curve for ground state[7] has been researched, while that for excited states has not been studied yet. The SAC/SAC-CI method,[8−12] which was originally published in 1978 for the study mainly on excited, ionized and electron-attached states of molecules, has been adopted to calculate various molecules successfully. Therefore, it is feasible to research the potential energy curves for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule with this method.

By optimizing the structures for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule with this method, doing the group sum of operators (GSUM[13]) scan calculations and fitting the Murrell–Sorbie functions for these electronic states, we calculate the spectroscopic constants (ω_e, $\omega_e\chi_e$, B_e, α_e) for each state. The calculated results are in good agreement with the experimental data. They provide the theoretical foundations for the research of the molecular reaction dynamics of SiO material.

*Project supported by the Basic Research Program of Education Bureau of Henan Province of China (Grant No 2008A140006).
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2. Theoretical method

In order to describe the APEF of molecule, a four-parameter Murrell–Sorbie function[14−16] has been used and the expression is

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

where, $\rho = R - R_e$, R is the internuclear distance of the diatomic molecule, R_e is its equilibrium internuclear distance and is regarded as a fixed parameter in the fitting process. The dissociation energy D_e and parameters a_1, a_2, a_3 are determined by fitting. The quadratic, cubic and quartic force constants f_2, f_3, f_4 have been derived from Eq.(1) and are as follows:

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

$$f_3 = -6D_e(a_3 - a_1a_2 + a_1^3/3), \quad (3)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3). \quad (4)$$

For diatomic molecule, the force constants f_2, f_3, f_4 can be educed[17,18] with the spectroscopic constants ω_e, $\omega_e\chi_e$, B_e, α_e and the equilibrium internuclear distance R_e:

$$f_2 = 4\pi^2\mu\omega_e^2c^2, \quad (5)$$

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

$$f_4 = \frac{f_2}{R_e^2}\left[15\left(1 + \frac{\alpha_e\omega_e}{6B_e^2}\right)^2 - \frac{8\omega_e\chi_e}{B_e}\right], \quad (7)$$

where c is the velocity of light, μ is the reduced mass of diatomic molecule, and the value of B_e is obtained by

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

From Eqs.(2)–(8), the following expressions[19] can be obtained:

$$\omega_e = \left[\frac{D_e(a_1^2 - 2a_2)}{4\pi^2\mu c^2}\right]^{\frac{1}{2}}, \quad (9)$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right], \quad (10)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{f_3R_e}{3f_2}\right), \quad (11)$$

$$B_e = \frac{h}{8\pi^2c\mu R_e^2}. \quad (12)$$

3. Results and discussions

All calculations are carried out using the SAC/SAC-CI method presented in the Gaussian03 program package.[20] The structures are optimized for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule with the SAC/SAC-CI method and different basis sets which are D95++, 6-311++G and 6-311++G**, and the results of optimization are listed in Table 1.

Table 1. Optimizational R_e(nm) for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO.

States	D95++	6-311++G	6-311++G**	Exp.[21]
$X^1\Sigma^+$	0.1586	0.1575	0.1512	0.1510
$A^1\Pi$	0.1734	0.1729	0.1627	0.1620
$C^1\Sigma^-$	0.1846	0.1830	0.1721	0.1727

According to Table 1, the basis set 6-311++G** has given the best optimizational results for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule. Especially, the value of R_e for $X^1\Sigma^+$ state is much more approximate to the experimental data[21] than 0.149 nm derived from Ref.[7] and 0.1519 nm derived from Ref.[22]. Then the GSUM scan calculations of SAC/SAC-CI method are carried out and a series of potential energy points are gained.

With an exact fit of calculational energies to a four-parameter Murrell–Sorbie function, the APEFs for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states are obtained. Based on the APEFs, we calculate the values of parameters of Murrell–Sorbie function, which are D_e, a_1, a_2, a_3 and the force constants f_2, f_3, f_4, and then list them in Table 2.

Table 2. The M–S parameters and force constants for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$states of SiO.

States		D_e/eV	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	f_2/aJ·nm^{-2}	f_3/aJ·nm^{-3}	f_4/aJ·nm^{-4}
	SAC	9.236	35.81	252.4	1063	1150.973	–65131.06	2907207.4
$X^1\Sigma^+$	Ref.[7]	9.511	38.46	175.6	1611	17.188	–788.68	4692.7
	Exp.[21]	8.337	32.08	168.5	1217	···	···	···
$A^1\Pi$	SAC-CI	3.569	38.16	212.6	556	589.568	–37624.10	1804472.0
$C^1\Sigma^-$	SAC-CI	2.431	43.69	412.4	1533	422.232	–26444.17	1204613.0

According to Table 2, the results of D_e, a_1 and a_3 for $X^1\Sigma^+$ state are in good agreement with the experimental data. The disparities of force constants f_2, f_3, f_4 between this work and Ref.[7] are large for $X^1\Sigma^+$ state. However, these results are believed to be accurate since the spectroscopic constants calculated by f_2, f_3, f_4 are in good agreement with the experimental data. So far, the experimental data for $A^1\Pi$ and $C^1\Sigma^-$ states have not yet been found. The potential energy curves with these states obtained from SAC/SAC-CI calculations are shown in Fig.1.

According to Fig.1, the dissociation energy obtained from energy scanning for each state is consistent quite well with the result obtained from fitting and the APEFs on the whole are in good agreement with *ab initio* values. It shows that the Murrell–Sorbie function is suitable for the description of potential energy curves of diatomic molecule and the SAC/SAC-CI method can be applied to the study of the potential energy curves for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule. In order to test the accuracy of APEFs for these electronic states, the spectroscopic constants for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states are calculated using Eqs.(9)–(12). They are listed in Table 3.

Table 3 shows the comparison of our spectroscopic constants with the experimental data. The relative errors of ω_e, $\omega_e\chi_e$, α_e and B_e between our results and experimental data are 11.5%, 2.5%, 1.2% and 14.0% for $X^1\Sigma^+$ state, 16.3%, 19.9%, 2.5% and 7.5% for $A^1\Pi$ state, 13.4%, 78.7%, 3.1% and 15.4% for $C^1\Sigma^-$ state respectively. Obviously, the results obtained by SAC/SAC-CI method for these states are nearly consistent with the experimental data. What is more, the calculations for the ground state $X^1\Sigma^+$ are more approximate to experimental data[21] than those in Ref.[7].

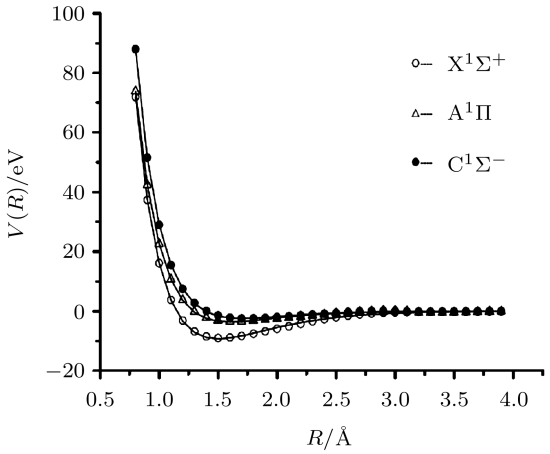


Fig.1. Potential energy curves for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO. Solid curve: fitting result; ○Δ●: scanned result (1 Å= 0.1 nm).

Table 3. Spectroscopic constants for $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO.

States		$\omega_e/\mathrm{cm}^{-1}$	$\omega_e\chi_e/\mathrm{cm}^{-1}$	B_e/cm^{-1}	$\alpha_e/\mathrm{cm}^{-1}$
	SAC	1385.1	5.82	0.736	0.0043
$X^1\Sigma^+$	Ref.[7]	1426.1	2.68	0.746	0.0030
	Exp.[21]	1241.6	5.97	0.727	0.0050
	SAC-CI	991.4	7.71	0.647	0.0061
$A^1\Pi$	Exp.[21]	852.8	6.43	0.631	0.0066
	SAC-CI	839.0	7.63	0.573	0.0060
$C^1\Sigma^-$	Exp.[21]	740.0	4.27	0.556	0.0052

4. Conclusions

The APEFs of $X^1\Sigma^+$, $A^1\Pi$ and $C^1\Sigma^-$ states of SiO molecule have been calculated by using SAC/SAC-CI method and have been used to compute the spectroscopic constants and force constants. Favourable agreement is found in comparison with the experimental data, which implies that the present work is more competent and in better agreement than previous studies. This proves that the Murrell–Sorbie function is suitable for the description of potential energy curves of diatomic molecule, and the SAC/SAC-CI method is effective for the study of ground and lower excited states of diatomic molecule. The results obtained here provide the theoretical foundations for the research of the molecular reaction dynamics of SiO material.

References

[1] Matsunaga N and Zavitsas A A 2004 *J. Chem. Phys.* **120** 5624

[2] Grandinetti F and Vinciguerra V 2002 *Int. J. Mass Spectrom.* **216** 286

[3] Zivy O and Czemek J 1999 *Chem. Phys. Lett.* **308** 165

[4] Hirst D M 2001 *J. Chem. Phys.* **115** 9320

[5] Horst M A T, Schatz G C and Harding L B 1996 *J. Chem. Phys.* **105** 558

[6] Liu Y J, Huang M B, Zhou X G *et al* 2002 *J. Chem. Phys.* **117** 6573

[7] Wu D L, Zeng X F, Ruan W, Zhao J, Cheng X L and Yang X D 2006 *Chin. J. Sichuan Normal University* (Natural Science) **29** 485 (in Chinese)

[8] Nakatsuji H 1978 *Chem. Phys. Lett.* **59** 362

[9] Nakajima T and Nakatsuji H 1999 *Chem. Phys.* **242** 177

[10] Ishida M, Toyota K, Ehara M and Nakatsuji H 2001 *Chem. Phys. Lett.* **347** 493

[11] Nakatsuji H 1979 *Chem. Phys. Lett.* **67** 329

[12] Nakatsuji H 1979 *Chem. Phys. Lett.* **67** 334

[13] Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa I, Ishida M, Nakajima T, Honda Y, Kitao O and Nakai H 2005 *SAC/SAC-CI program combined with Gaussian for calculating ground, excited, ionized, and electron-attached states and singlet, doublet, triplet, quartet, quintet, sextet and septet spin states and their analytical energy gradients* (Kyoto: Kyoto University)

[14] Murrell J N and Sorbie K S 1974 *J. Chem. Soc. Faraday Trans.* **70** 1552

[15] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Function* (Beijing: Science Press) Chapter 4 (in Chinese)

[16] Yan S Y and Xu G L 2007 *Chin. Phys.* **16** 686

[17] Dunham J L 1932 *Phys. Rev.* **41** 721

[18] Shi D H, Sun J F, Zhu Z L, Ma H and Yang X D 2008 *Acta Phys. Sin.* **57** 165 (in Chinese)

[19] Shi D H, Sun J F, Zhu Z L and Liu Y F 2007 *Chin. Phys.* **16** 2701

[20] Frisch M J, Trucks G W, Schlegel H B *et al.* 2003 *Gaussian 03, RevisionB.02* (Pittsburgh PA: Gaussian Inc.)

[21] Huber K P and Herzberg G 1978 *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold)

[22] Xu G L, Liu Y F, Sun J F, Zhang X Z and Zhu Z H 2007 *Acta Phys. Sin.* **56** 5704 (in Chinese)