The theoretical study on the potential energy curve for $X^3\Delta$ state of TiO molecule*

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This paper applies the density functional theory method to optimise the structure for $X^3\Delta$ state of TiO molecule with the basis sets 6-31G, 6-31++G and 6-311G**. Comparing the attained results with the experiments, it obtains the conclusion that the basis set 6-31++G is most suitable for the optimal structure calculations of $X^3\Delta$ state of TiO molecule. The whole potential energy curve for the electronic state is further scanned by using B3P86/6-31++G method for the ground state, then it uses a least square fitted to Murrell–Sorbie functions, at last it calculates the spectroscopic constants and force constants, which are in better agreement with the experimental data.

Keywords: B3P86, TiO, potential energy function, spectroscopic constants
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1. Introduction

Quantitative molecular spectroscopic knowledge can be derived from the molecular analytic potential energy function, therefore, it is necessary to set reliable physical models of bonding potentials. With the development of modern quantum chemical methods and the improvement of computer calculating speed, numerous theoretical models and algorithmic progress have been made to take advantage of large inexpensive computer storage devices as well as enhanced parallel programming methods, so we can obtain more credible results based on higher computational levels. And *ab initio* can give progressively more accurate potential energy curves, especially for the small molecules.

The TiO is the most abundant of the 3d oxides presented in the spectra of cool M and S class stars,[1] it is used for spectral classification of these stars.[2,3] The distribution of intensities in the rotational structure of TiO bands is a test to determine the temperature of stellar atmospheres.[4−6] The TiO can dominate the spectra of M-type stars if it is metal-rich, which can arise from recycled supernova material. The spectra is further complicated by numerous perturbations between states and large nuclear spins and magnetic moments. In addition, the quasi-bound Rydberg resonances of the TiO complex are presented in photon or electron collisional excitation cross sections. On the other hand, the molecular potential energy function is the complete description of the molecular electronic structure[7−12] and the foundation for the molecular reaction dynamics study, and it is more important to understand the structure and properties of TiO. For TiO molecule, the structure parameters and some spectral data have been obtained by experimental and theoretical research,[13,14] while the potential energy function of the ground state of TiO has not been reported in the previous papers.

By optimising the structure for the ground state ($X^3\Delta$) of TiO molecule with B3P86 method, doing the scan calculations and fitting the Murrell–Sorbie functions for the electronic state, the spectroscopic constants (ω_e, $\omega_e\chi_e$, B_e, α_e) for the ground state ($X^3\Delta$) are calculated. The calculated results are in better agreement with the experimental data than those in Ref. [13], and provide the theoretical foundations for the research of the potential energy function and dynamic parameters of TiO material.

2. Theoretical method

It is well known that analytical potential energy functions of different electronic states are different and

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states dissociating in different channels are different. To deduce molecular analytical potential energy function, the molecular electronic states and the atomic states after dissociation, i.e. dissociation limits, have to be determined first, otherwise we cannot obtain correct potential energy functions. By employing the principles of atomic and molecular reaction statics, we can deduce the molecular dissociation limits.

The ground state ($X^3\Delta$) of TiO dissociates adiabatically into two ground states O and Ti atoms, so its equilibrium configuration is $C_{\infty v}$. According to the group theoretical derivation of molecular electronic states, we resolve the atomic group representations into $C_{\infty v}$ because the TiO molecule has $C_{\infty v}$ symmetry. Then the direct products of $C_{\infty v}$ representations of the two atoms are the possible states of the molecule. The ground state of O is ${}^3P_g$ and that of Ti is (${}^3F_{\rm g}$, ${}^3P_{\rm g}$, ${}^3G_{\rm g}$, ${}^3D_{\rm g}$, ${}^3S_{\rm g}$),

and

$$
\begin{aligned}
&{}^3F_{\rm g}\rightarrow {}^3\Sigma^- \oplus {}^3\Pi \oplus {}^3\Delta \oplus {}^3\Phi,\\
&{}^3P_{\rm g}\rightarrow {}^3\Sigma^- \oplus {}^3\Pi,\\
&{}^3G_{\rm g}\rightarrow {}^3\Sigma^+ \oplus {}^3\Pi \oplus {}^3\Delta \oplus {}^3\Phi \oplus {}^3\Gamma,\\
&{}^3S_{\rm g}\rightarrow {}^3\Sigma^+.
\end{aligned}
$$

Their dissociation limits are:

$$
\begin{aligned}
&({}^3\Sigma^- \oplus {}^3\Pi \oplus {}^3\Delta \oplus {}^3\Phi) \otimes ({}^3\Sigma^- \oplus {}^3\Pi) \rightarrow {}^{1,3,5}\Delta \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\Sigma^+ \oplus {}^{1,3,5}[\Sigma^-] \oplus {}^{1,3,5}\Sigma^+\\
&\oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\phi \oplus {}^{1,3,5}\Delta \oplus {}^{1,3,5}\Gamma, \qquad (1)\\
&({}^1\Sigma^+ \oplus {}^1\Pi \oplus {}^1\Delta \oplus {}^1\Phi \oplus {}^1\Gamma) \otimes ({}^3\Sigma^- \oplus {}^3\Pi) \rightarrow {}^3\Sigma^- \oplus {}^3\Pi \oplus {}^3\Delta \oplus {}^3\Phi \oplus {}^3\Gamma \oplus ({}^2\Gamma \otimes {}^3\Pi), \qquad (2)\\
&({}^3\Sigma^- \oplus {}^3\Pi) \otimes ({}^3\Sigma^- \oplus {}^3\Pi) \rightarrow {}^{1,3,5}\Sigma^+ \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\Sigma^+ \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}[\Sigma^-] \oplus {}^{1,3,5}\Delta, \qquad (3)\\
&({}^1\Sigma^+ \oplus {}^1\Pi \oplus {}^1\Delta \otimes ({}^3\Sigma^- \oplus {}^3\Pi) \rightarrow {}^3\Sigma^+ \oplus {}^3\Pi \oplus {}^3\Delta \oplus {}^3\Pi \oplus {}^3\Sigma^+ \oplus [\Sigma^-] \oplus {}^3\Delta \oplus {}^3\Pi \oplus {}^3\Phi, \qquad (4)\\
&{}^1\Sigma^+ \otimes ({}^3\Sigma^- \oplus {}^3\Pi) \rightarrow {}^3\Sigma^- \oplus {}^3\Pi. \qquad (5)
\end{aligned}
$$

Using density function theory we find that the ground state of TiO is $X^3\Delta$. So the possible ground state of TiO corresponding to the dissociation limit is

$$
{}^{1,3,5}\Delta \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\Sigma^+ \oplus {}^{1,3,5}[\Sigma^-] \oplus {}^{1,3,5}\Sigma^+ \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\Pi \oplus {}^{1,3,5}\Phi \oplus {}^{1,3,5}\Delta \oplus {}^{1,3,5}\Gamma.
$$

According to the principle of reversibility for the microscopic process, the dissociation limit of TiO ($X^3\Delta$) is

$$
{\rm TiO}(X^3\Delta) \rightarrow {\rm O}({}^3P_{\rm g}) + {\rm Ti}({}^3F_{\rm g}).
$$

In order to describe the analytic potential energy function of molecule, a four-parameter Murrell–Sorbie function[15–17] has been used and the expression is

$$
V(\rho) = -D_{\rm e}(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho), \qquad (6)
$$

where $\rho = R - R_{\rm e}$, R is the internuclear distance of the diatomic molecule and $R_{\rm e}$ is its equilibrium internuclear distance and is regarded as a fixed parameter in the fitting process. The dissociation energy $D_{\rm e}$ 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:

$$
f_2 = D_{\rm e}(a_1^2 - 2a_2), \qquad (7)
$$

$$
f_3 = -6D_{\rm e}(a_3 - a_1a_2 + a_1^3/3), \qquad (8)
$$

$$
f_4 = D_{\rm e}(3a_1^4 - 12a_1^2a_2 + 24a_1a_3). \qquad (9)
$$

For diatomic molecule, the force constants f_2, f_3, f_4 can be educed[18,19] with the spectroscopic constants $\omega_{\rm e}$, $\omega_{\rm e}\chi_{\rm e}$, $B_{\rm e}$, $\alpha_{\rm e}$ and the equilibrium internuclear distance $R_{\rm e}$ as follows:

$$
f_2 = 4\pi^2\mu\omega_{\rm e}^2c^2, \qquad (10)
$$

$$
f_3 = -\frac{3f_2}{R_{\rm e}}\left(1 + \frac{\alpha_{\rm e}\omega_{\rm e}}{6B_{\rm e}^2}\right), \qquad (11)
$$

$$
f_4 = \frac{f_2}{R_{\rm e}^2}\left[15\left(1 + \frac{\alpha_{\rm e}\omega_{\rm e}}{6B_{\rm e}^2}\right)^2 - \frac{8\omega_{\rm e}\chi_{\rm e}}{B_{\rm e}}\right], \qquad (12)
$$

where, c is the velocity of light, μ is the reduced mass of diatomic molecule, and the value of $B_{\rm e}$ is obtained by

$$
B_{\rm e} = \frac{h}{8\pi^2c\mu R_{\rm e}^2}. \qquad (13)
$$

From Eqs. (7)–(13), the following expressions[20,21] can be obtained:

$$
\omega_{\rm e} = \left[\frac{D_{\rm e}(a_1^2 - 2a_2)}{4\pi^2\mu c^2}\right]^{1/2}, \qquad (14)
$$

$$
\omega_{\rm e}\chi_{\rm e} = \frac{B_{\rm e}}{8}\left[-\frac{f_4R_{\rm e}^2}{f_2} + 15\left(1 + \frac{\omega_{\rm e}\alpha_{\rm e}}{6B_{\rm e}^2}\right)^2\right], \qquad (15)
$$

$$\alpha_{\rm e} = -\frac{6B_{\rm e}^2}{\omega_{\rm e}}\left(1+\frac{f_3 R_{\rm e}}{3f_2}\right), \quad (16)$$

$$B_{\rm e} = \frac{h}{8\pi^2 c\mu R_{\rm e}^2}. \quad (17)$$

3. Results and discussions

All calculations are carried out by using the B3P86 method presented in the Gaussian 03 programme package.[22] The structure is optimised for $X^3\Delta$ state of TiO molecule with the B3P86 method and different basis sets, which are 6-31G, 6-31++G, 6-311G**, and the results of optimisation are listed in Table 1.

According to Table 1, the basis set 6-31++G has given the best optimised results for $X^3\Delta$ state of TiO molecule. Especially, the value of $D_{\rm e}$ for the ground state is much more approximate to the experimental data[14] than 6.64 eV derived from Ref. [13]. Then the scan calculations of B3P86/6-31++G method are carried out and a series of potential energy points are gained.

Table 1. Optimised $R_{\rm e}$ (nm), $D_{\rm e}$ (eV) for $X^3\Delta$ state of TiO.

state	6-31G		6-31++G		6-311G**		Exp. [14]	
	$R_{\rm e}$/nm	$D_{\rm e}$/eV	$R_{\rm e}$/nm	$D_{\rm e}$/eV	$R_{\rm e}$/nm	$D_{\rm e}$/eV	$R_{\rm e}$/nm	$D_{\rm e}$/eV
$X^3\Delta$	0.16216	7.42	0.16321	6.74	0.15905	7.22	0.16202	6.87

With an exact fit of calculational energies to Murrell–Sorbie function, the analytical potential energy function for $X^3\Delta$ state is obtained. Based on the analytic potential energy function, the values of parameters of Murrell–Sorbie function, which are a_1, a_2, a_3 and the force constants f_2, f_3, f_4 are calculated, and then listed in Table 2.

Table 2. The M–S parameters and force constants for $X^3\Delta$ state of TiO.

state	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})
$X^3\Delta$	19.9067	–138.520	442.07	726.696	–37747.15	1447331.9

So far, the experimental data a_1, a_2, a_3, and f_2, f_3, f_4 for $X^3\Delta$ state have not yet been found. 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. The potential energy curve with the state obtained from B3P86/6-31++G calculations is shown in Fig. 1.

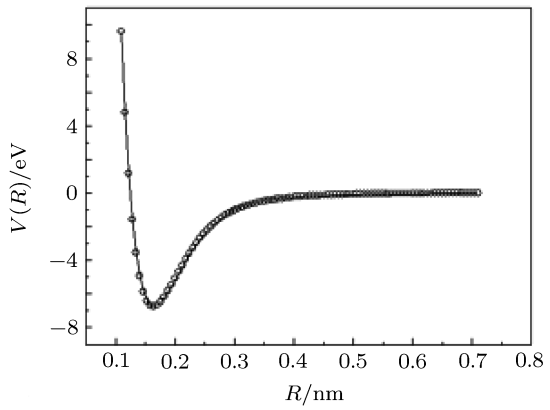


Fig. 1. Potential energy curve for $X^3\Delta$ state of TiO. Solid curve: fitting result; ◯: scanned result.

According to Fig. 1, the dissociation energy obtained from energy scanning for the ground state is consistent with the result obtained from fitting quite well and the analytical potential energy function is in good agreement with *ab initio* values on the whole. It shows that the Murrell–Sorbie function is suitable for the description of potential energy curve of diatomic molecule and the B3P86/6-31++G method can be applied to the study of the potential energy curve for $X^3\Delta$ state of TiO molecule. In order to test the accuracy of analytical potential energy function for the electronic state, the spectroscopic constants for $X^3\Delta$ state are calculated by using Eqs. (14)–(17). They are listed in Table 3.

The numbers in Table 3 show the comparison of our spectroscopic constants with the experimental data. The relative errors of $\omega_{\rm e}$, $\omega_{\rm e}\chi_{\rm e}$, $B_{\rm e}$ and $\alpha_{\rm e}$ between our results and experimental data are 0.4%, 2.17%, 1.4%, 0.1 % for $X^3\Delta$ state respectively. Obviously, the results obtained by B3P86/6-31++G method for the ground state ($X^3\Delta$) are nearly consistent with the experimental data. What is more, the conclusions for the ground state ($X^3\Delta$) is more approximate to experimental data[14] than those in Ref. [13].

Table 3. Spectroscopic constants for $X^3\Delta$ state of TiO.

method	ω_e/cm^{-1}	$\omega_e\chi_e/cm^{-1}$	α_e/cm^{-1}	B_e/cm^{-1}	D_e/eV
B3P86	1013.8	4.40	0.003005	0.52738	6.74
Ref. [13]	1014	—	—	—	6.64
Exp.[14]	1009.02	4.498	0.00301	0.53541	6.87

4. Conclusions

The analytical potential energy functions of $X^3\Delta$ state of TiO molecule have been calculated by using B3P86/6-31++G 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 TiO molecule, and the B3P86 method is effective for the study of ground state of TiO molecule. The results obtained here provide the theoretical foundations for the research of the structure and the nature of TiO material.

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