Theoretical study of the structure and analytic potential energy function for the ground state of the PO_2 molecule*

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In this paper, the energy, equilibrium geometry, and harmonic frequency of the ground electronic state of PO_2 are computed using the B3LYP, B3P86, CCSD(T), and QCISD(T) methods in conjunction with the 6-311++G(3df, 3pd) and cc-pVTZ basis sets. A comparison between the computational results and the experimental values indicates that the B3P86/6-311++G(3df, 3pd) method can give better energy calculation results for the PO_2 molecule. It is shown that the ground state of the PO_2 molecule has C_{2v} symmetry and its ground electronic state is X^2A_1. The equilibrium parameters of the structure are $R_{P-O} = 0.1465$ nm, $\angle OPO = 134.96°$, and the dissociation energy is $E_d = 19.218$ eV. The bent vibrational frequency $\nu_1 = 386$ cm^{-1}, symmetric stretching frequency $\nu_2 = 1095$ cm^{-1}, and asymmetric stretching frequency $\nu_3 = 1333$ cm^{-1} are obtained. On the basis of atomic and molecular reaction statics, a reasonable dissociation limit for the ground state of the PO_2 molecule is determined. Then the analytic potential energy function of the PO_2 molecule is derived using many-body expansion theory. The potential curves correctly reproduce the configurations and the dissociation energy for the PO_2 molecule.

Keywords: PO_2, Murrell–Sorbie function, many-body expansion theory, potential energy curve

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1. Introduction

The molecular potential energy function is the eigenenergy function of the electron under the Born–Oppenheimer approximation. From a dynamic point of view, constructing reliable analytical potential functions, which is the basis for studying the atomic and molecular collision and the molecular reaction dynamics,[1−3] will help us understand the dissociation processes in different reaction channels more thoroughly. The PO_2 radical is well known, since it is easily generated by the phosphorus–oxygen reaction, and it is also an important intermediate in discharge environments containing PO_3, P_2O_5, and P_2O_4. In recent years, there has been an increasing interest in understanding the chemistry of PO_2, and the spectrum of the ground state PO_2 molecule (X^2A_1) has been extensively investigated by various high-resolution spectroscopic methods.[4−10] Besides the experimental studies, many theoretical investigations have been reported in the literature[11−15] about the equilibrium geometry of the ground state of PO_2 (X^2A_1). Lohr[11] calculated the equilibrium geometries of X^2A_1 at the UHF/6-31G* level. Later on, Lohr and Boehm[12] calculated the vibrational frequencies of X^2A_1 at the RHF/6-31g + d level. Using the self-consistent field (SCF) and the multi-configuration self-consistent field (MCSCF) methods, Kabbadj and Lievin[13] evaluated the equilibrium geometries, vibrational frequencies, and adiabatic excitation energies for low-lying electronic states of PO_2. Jarrett-Sprague *et al.*[14] reported the structure and infrared spectrum of PO_2 at the RHF/6-31g* level. Xu *et al.*[15] obtained the equilibrium geometry and the vibrational frequencies of PO_2 to analyze the photoelectron spectroscopic data, and Cai *et al.*[16] used the multi-reference double-excitation configuration interaction (MRD-CI) method to calculate the geometries, adiabatic excitation energies, force constants, and vibrational frequencies of the ground state and three lowest-lying PO_2 electronic excited states. By comparing with the theoretical and the experimental results listed above, they found their calculations to be more accurate. However, up to now, to the best of our knowledge, the potential function and the contours of potential curves for the PO_2 (X^2A_1) molecule in

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many-body expansion form, which are of great importance in molecular reaction dynamics research, have not been reported in the literature.

In the present work, in order to explore the PO_2 molecule, we calculate the equilibrium geometry, dissociation energy, and force constants for PO_2 (X^2A_1) at the chosen B3P86/6-311++G(3df, 3pd) level. Using the atomic and molecular reaction statics,[17] we derive a reasonable dissociation limit for the ground state of the PO_2 molecule. In light of the results, we extend the many-body expansion to obtain the analytical potential energy function of PO_2 (X^2A_1). To emphasize it, we also depict the contours of the potential energy function of PO_2 (X^2A_1). In order to examine whether the present calculations improve over the previous results and give the direction for the experimental research, all the calculations are compared with the previous theoretical and experimental results.

2. Computational details

2.1. The electronic state and dissociation limit of PO_2 (X^2A_1)

The full space potential energy function for a triatomic system is the basis of molecular reaction dynamics. Based on quantum mechanical calculation, the ground electronic state of PO_2 for alpha orbital occupied is (A_1) (A_1) (B_2) (A_1) (B_1) (A_1) (B_2) (A_1) (B_2) (A_1) (B_2) (A_1) (B_1) (A_2) (B_2) (A_1), and for beta orbital occupied is (A_1) (B_2) (A_1) (A_1) (B_1) (B_2) (A_1) (A_1) (B_2) (A_1) (B_2) (B_1) (A_1) (A_2) (B_2). So the ground electronic state of PO_2 is X^2A_1.

According to the principle of microscopic reversibility in the atomic and molecular reaction statics, the possible dissociation processes for the PO_2 molecule can be expressed as

$$PO_2(X^2A_1) \rightarrow \begin{cases} O(^3P_g) + PO(X^2\Pi), \\ O_2(X^3\Sigma^-) + P(^4S_u), \\ O(^3P_g) + O(^3P_g) + P(^4S_u). \end{cases} \quad (1)$$

2.2. Equilibrium geometry of PO_2 (X^2A_1)

All the *ab initio* calculations are performed using the GAUSSIAN 03 program package.[18] Quantum chemical methods B3LYP, B3P86, CCSD(T), and QCISD(T), in conjunction with 6-311++G(3df, 3pd) and the cc-pVTZ basis sets, are employed to compute the equilibrium geometric structure and the harmonic frequencies of the PO_2 (X^2A_1) molecule. The calculated results are all listed in Table 1. The results of the previous theoretical calculations and experimental results are also given for comparison.

Table 1. Comparison of calculated molecular geometric parameters at equilibrium for the ground state of PO_2 (X^2A_1).

Method	$E^{a)}$/a.u.	R_{P-O}/nm	∠OPO/(°)	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}
B3P86/6-311++G(3df, 3pd)	–492.431572	0.1465	134.96	1095	386	1333
B3LYP/6-311++G(3df, 3pd)	–491.880507	0.1470	135.54	1078	390	1365
CCSD(T)/6-311++G(3df, 3pd)	–491.1597577	0.1471	135.94	1073	387	1357
QCISD(T)/6-311++G(3df, 3pd)	–491.1627458	0.1473	135.98	1068	383	1348
B3P86/cc-pVTZ	–492.425640	0.1476	133.75	1087	386	1307
B3LYP/cc-pVTZ	–491.873384	0.1481	133.32	1069	390	1339
CCSD(T)/cc-pVTZ	–491.143276	0.1482	134.67	1067	389	1356
QCISD(T)/cc-pVTZ	–491.157210	0.1484	134.72	1053	384	1322
(MRD-CI/TZ+2d+R)[b)]	–491.04208	0.1464	135.14	1052	389	1338
Exp.[c)]	–	0.1467±0.0004	135.3±0.8	1117±20	387±20	1278
Exp.[d)]	–	–	–	–	386.4	1319.1

[a)]Zero-point energies are taken into account. [b)]Ref. [16], [c)]Ref. [4], [d)]Ref. [11].

From Table 1, comparing the present computational results with the experimental values available, we can find that the B3P86/6-311++G(3df, 3pd) method can be used to produce better results for the structure optimization and the frequency calculation of the PO_2 molecule. It is noteworthy to point out that Cai *et al.*[16] calculated the equilibrium parameters of the X^2A_1 ground state at the MRD-CI/TZ+2d+R level and concluded that their results were in better agreement with the available experimental values[4,11] than the other previous theoretical calculations.[10–14] As can be seen in Table 1, the calculated results in this work present some improvements over the geometric calculations of Cai *et al.*[16]

The computational results show that the ground symmetry of PO_2 belongs to point group C_{2v}. The bond length is $R_{P-O} = 0.1465$ nm, and the bond angle is $\angle OPO = 134.96°$. Vibrational frequencies are as follows: the bent vibrational frequency is $\nu_1 = 386$ cm^{-1}, the symmetric stretching frequency is $\nu_2 = 1095$ cm^{-1}, and the asymmetric stretching frequency is $\nu_3 = 1333$ cm^{-1}.

In order to determine the dissociation energy of PO_2 (X^2A_1) corresponding to the reasonable dissociation limit $PO_2(X^2A_1) \rightarrow O(^3P_g) + O(^3P_g) + P(^4S_u)$ at the B3P86/6-311++G(3df, 3pd) level, we first calculate the total energy including the zero-point correction energy of PO_2 to be $E(PO_2)$=−492.431572 a.u. Then the total energies for the ground states of $O(^3P_g)$ and $P(^4S_u)$ are evaluated at the same level to be −74.117805 a.u. and −341.489424 a.u., respectively. So the dissociation energy of PO_2 (X^2A_1) is $E_d = E(P) + 2E(O) - E(PO_2) = 19.218$ eV. All the equilibrium geometry, force constants, and vibrational frequencies are listed in Table 2.

Table 2. Equilibrium structural parameters and force constants for PO_2 (X^2A_1).

Bond distance/nm	$R_{P-O} = 0.1465$
	$R_{O-O} = 0.2706$
Bond angle/(°)	$\angle OPO = 134.96$
Dissociation energy/eV	$E_d = 19.218$
Force constants/a.u.	$f_{RR} = f_{rr} = 0.61855$
	$f_{Rr} = 0.01947$
	$f_{R\theta} = f_{r\theta} = 0.02714$
	$f_{\theta\theta} = 0.19964$

2.3. Analytical potential energy functions and spectroscopic constants for PO and O_2 molecules

Geometry optimizations for the ground states of PO ($X^2\Pi$) and O_2 ($X^3\Sigma^-$) molecules are conducted at the chosen computational level B3P86/6-311++G(3df, 3pd). Each optimized structure is confirmed by the frequency calculation to be the real energy minimum with no imaginary vibrational frequency. The whole analytic potential energies for the ground electronic states of PO ($X^2\Pi$) and O_2($X^3\Sigma^-$) molecules are further scanned using the same method. The potential energy functions and the relevant spectroscopic constants are then obtained by least square fitting to the Murrell–Sorbie function[19]

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

where $\rho = R - R_e$, with R being the diatomic internuclear distance, R_e being its equilibrium internuclear distance and regarded as a fixed parameter in the fitting process in this paper; E_d is the dissociation energy; and a_i are the parameters determined by the fitting. For the Murrell–Sorbie function, the quadratic, cubic, and quartic force constants can be derived from the following equations:

$$f_2 = E_d(a_1^2 - 2a_2), \quad (3)$$

$$f_3 = -6E_d\left(a_3 - a_1a_2 + \frac{1}{3}a_1^2\right), \quad (4)$$

$$f_4 = E_d(3a_1^4 - 12a_1^2a_2 + 24a_1a_3). \quad (5)$$

And then, the spectroscopic parameters are

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad (6)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}, \quad (7)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{f_3R_e}{3f_2}\right), \quad (8)$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right], \quad (9)$$

where μ is the reduced mass of diatomic molecules PO and O_2; c is the speed of light in vacuum; and B_e, α_e, ω_e, and $\omega_e\chi_e$ represent the rigid-rotational factor, nonrigid-rotational factor, harmonic vibrational frequency, and inharmonic vibrational factor, respectively.

The fitting parameters of the potential energy functions and the spectroscopic parameters for PO ($X^2\Pi$) and O_2 ($X^3\Sigma^-$) molecules are listed in Tables 3 and 4, respectively. All the available experimental data[19] of the spectroscopic parameters are also displayed in Table 4 for comparison. As can be seen in Table 4, the spectroscopic parameters obtained in this paper are in excellent accordance with the experimental values.[19]

Table 3. The parameters of the Murrell–Sorbie potential function and force constants for PO ($X^2\Pi$) and O_2 ($X^3\Sigma^-$) molecules.

Molecule	R_e/nm	E_d/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·J·nm^{-4}
PO	0.1474	6.226	42.75	439.9	2717	945.4153	–59576.334	3152432
O_2	0.1205	5.213	60.80	1147.7	11003	1170.3459	–80889.927	5127771

Table 4. The spectroscopic constants of the ground states of PO and O_2 molecules.

Molecule	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	E_d/cm^{-1}
PO	0.1474	1233.39	6.54	0.0053	0.0053	1.04×10^{-6}
Exp.[a)]	0.1476	1233.34	6.56	0.7337	0.0055	1.30×10^{-6}
O_2	0.1205	1576.00	9.43	1.4445	0.01416	4.45×10^{-6}
Exp.[a)]	0.1208	1580.19	11.98	1.4456	0.01593	4.84×10^{-6}

[a)] Ref. [19].

2.4. Many-body expansion analytical potential energy function of $PO_2(X^2A_1)$

Sorbie and Murrell[20] studied the potential energy functions of the polyatomic molecules and presented the many-body expansion theory,[20] which presents many advantages: meeting the requirement of molecular symmetry, including all possible relevant limits, and being reasonable physically. Based on the spectroscopic data, it can accurately present the potential energy surface, and is widely used in dynamical approaches. The potential energy surface of a triatomic molecule is a hypersurface in the three-dimensional space.[21−25] If we choose the energy of the ground state of the atom or ion as the reference energy, the many-body expansion analytical potential energy function of the ground state $PO_2(X^2A_1)$ molecule is

$$V(R_1,R_2,R_3) = V^2_{P-O}(R_1) + V^2_{P-O}(R_2) + V^2_{O-O}(R_3) + V^3_{O-P-O}(R_1,R_2,R_3), \quad (10)$$

where R_1=R_2=R_{P-O}, $R_3 = R_{O-O}$, $V^2_{P-O}(R_1)$, $V^2_{P-O}(R_2)$, and $V^2_{O-O}(R_3)$ denote the Murrell–Sorbie potential functions of the PO ($X^2\Pi$) and O_2 ($X^3\Sigma^-$) molecules. Now, we derive the three-body term

$$V^3_{O-P-O}(R_1,R_2,R_3) = PT, \quad (11)$$

where P is a polynomial, and T is a range function, which are given, respectively, by

$$P = C_0 + C_1S_1 + C_2S_3 + C_3S_2^2 + C_4S_3^2 + C_5S_1S_3 + C_6S_3^4 + C_7S_1^2 + C_8S_1(S_2^2+S_3^2) + C_9S_2S_3^2, \quad (12)$$

and

$$T = [1-\tanh(\gamma_1S_1/2)][1-\tanh(\gamma_2S_2/2)] \times [1-\tanh(\gamma_3S_3/2)]. \quad (13)$$

According to the structure optimization computational results of PO_2, we choose the C_{2v} symmetry (R_1=R_2=R_{P-O}=0.1465 nm, $R_3 = R_{O-O}$ = 0.2706 nm) as the reference structure. Then, the internal coordinates are $\rho_i = R_i - R_{ei}$ ($i = 1,2,3$), and the corresponding symmetrical internal coordinates are

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix}. \quad (14)$$

The linear parameters C_i ($i = 0,1,\ldots,9$) in Eq. (12) can be determined by using the equilibrium structure and the force constants listed in Table 2, and the nonlinear parameters (γ_1, γ_2, γ_3) in Eq. (13) can be evaluated by optimizing the potential energy surface. All the three-body term parameters in the analytical potential energy function for PO_2 (X^2A_1) are listed in Table 5.

Table 5. The three-body term parameters in the analytical potential energy function for PO_2 (X^2A_1).

C_0	0.977977	C_7	0.428854
C_1	2.847551	C_8	–9.756914
C_2	8.525721	C_9	–6.600007
C_3	–7.317821	γ_1	1.5
C_4	–2.817432	γ_2	1.5
C_5	5.704754	γ_3	1.5
C_6	–6.917669		

3. Results and discussion

In order to analyze the physical significance of the potential energy function for PO_2 (X^2A_1) more clearly and show its structure symmetry, we plot the contours of the PO_2 (X^2A_1) potential in Figs. 1–3. These figures accurately reproduce the equilibrium geometry of the PO_2 (X^2A_1) molecule.

Figure 1 shows the O–P and the P–O bond stretching contours for a fixed angle ∠OPO=134.96°. From this figure, we can find a potential well (−19.218 eV) at $R_{O-P} = R_{P-O} = 0.1465$ nm, which shows that a steady PO_2 molecule can easily form. Moreover, we can also see that there is no saddle point in the contour and no evident potential barrier exists

during the reaction. Therefore, reaction O+PO→PO_2 is a non-threshold energy reaction.

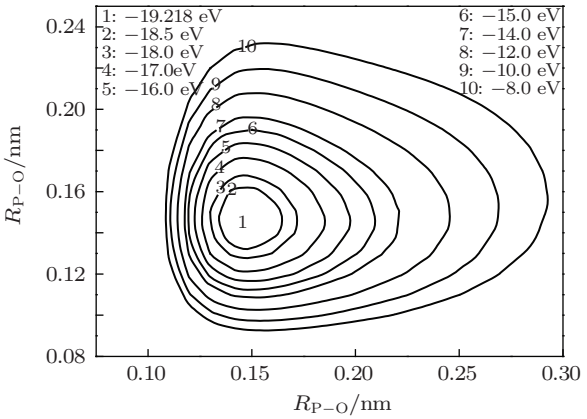


Fig. 1. The O–P and P–O bond stretching contours for $PO_2(X^2A_1)$.

Figure 2 shows the contour lines of PO_2 (X^2A_1) for the O atom moving around the fixed P–O bond ($R_{P-O} = 0.1465$ nm). We can see that the lowest energy is at point 1 (−19.218 eV). The contours clearly reproduce the C_{2v} symmetry of PO_2 (X^2A_1). Moreover, PO_2 can easily form if the O atom attacks the P–O bond from the side and the angle is about 134.96°. This is in accordance with the *ab initio* result.

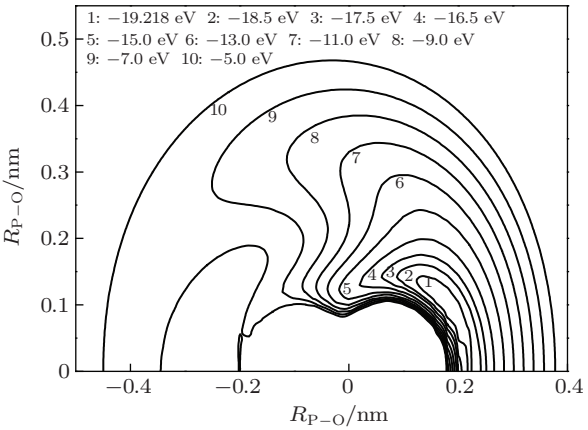


Fig. 2. Contour lines of PO_2 (X^2A_1) for the O atom moving around the P–O bond.

Figure 3 displays the contour lines of PO_2 (X^2A_1) for the P atom moving around the fixed O–O bond ($R_{O-O} = 0.2706$ nm). The PO_2 can easily form if the P atom attacks the O–O bond from the direction perpendicular to the O–O bond.

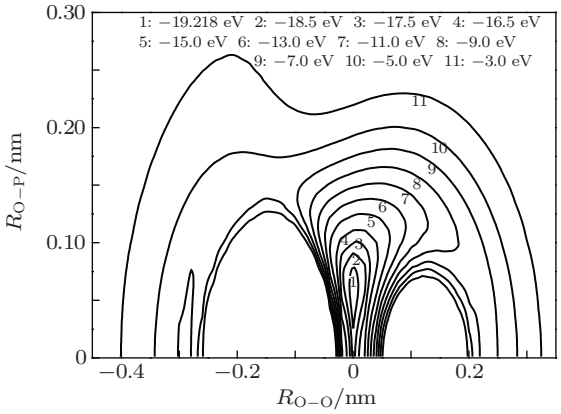


Fig. 3. Contour lines of PO_2 (X^2A_1) for the P atom moving around the O–O bond.

4. Conclusion

The chosen method, B3P86/6-311++G(3df, 3pd), is utilized to calculate the equilibrium geometry, force constants, and vibrational frequencies of PO_2 (X^2A_1). The calculated results show that the geometries and the vibrational frequencies in this work are in better agreement with the available experimental values than the previous theoretical results. At the same level, the analytical potential energy functions of the ground states for the PO and O_2 molecules are obtained by fitting the computational energies to the Murrell–Sorbie function, based on which the spectroscopic parameters and the force constants have been determined. According to the principle of atomic and molecular reaction statics, we first report the potential energy function of PO_2 (X^2A_1) with the many-body expansion theory. The contours of the potential energy function accurately and clearly reproduce the characteristics of the equilibrium geometry for the ground state PO_2 molecule.

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