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Potential energy surfaces of ozone in the ground state*

Shao Ju-Xiang(邵菊香)[a)b)†], Zhu Zheng-He(朱正和)[b)], Huang Duo-Hui(黄多辉)[a)]
Wang Jun(王 君)[b)], Cheng Xin-Lu(程新路)[b)], and Yang Xiang-Dong(杨向东)[b)]

[a)] *Department of Physics and Electronic Information, Laboratory of Computational Physics, Yibin University, Yibin* 644007, *China*

[b)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

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Equilibrium parameters of ozone, such as equilibrium geometry structure parameters, force constants and dissociation energy are presented by CBS-Q *ab initio* calculations. The calculated equilibrium geometry structure parameters and energy are in agreement with the corresponding experimental values. The potential energy function of ozone with a C_{2v} symmetry in the ground state is described by the simplified Sorbie–Murrell many-body expansion potential function according to the ozone molecule symmetry. The contour of bond stretching vibration potential of an O_3 in the ground state, with a bond angle (θ) fixed, and the contour of O_3 potential for O rotating around O_1–O (R_1), with O_1–O bond length taken as the one at equilibrium, are plotted. Moreover, the potentials are analysed.

Keywords: ozone, potential energy surface, barrier, dissociation energy
PACC: 0570L, 3620E, 3520G

1. Introduction

It is well known that ozone, particularly, in the upper atmosphere is crucial to life processes. Ozone is also important in syntheses,[1] environments,[2−5] chemistry and physics. So, its physical and chemical properties such as its structure, spectra, and thermal reactions, etc, have been extensively investigated.[6−20]

The *ab initio* studies[10−16] have revealed that an accurate calculation of the ozone potential function has already become a challenging problem about the ground electronic state. Xantheas *et al*[14] have indicated that the C_{2v} constrained potential energy surface (PES) of the $^1A_1$ ground state of ozone is pertinent to the opening of the D_{3h} ring. Müller *et al*[16] have calculated the dissociation energy of ozone ($\tilde{X}\,^1A_1$). Several empirical potential functions of ozone have been proposed so far,[17−19] and they can be divided into two classes. One is mainly to describe qualitatively the topographic features of the PES for all imaginable geometries (including those structures which are not stable at all) by using the information on inelastic scattering and thermal rate data of isotope exchange reactions,[17,18] and the other is devoted to the determination of the effective potential function of configurations in the neighbourhood of equilibrium.

It is well known that an ozone molecule has two types of minima: one is of C_{2v} symmetry (referred to as open minimum) and the other is of D_{3h} symmetry (ring minimum) in which the oxygen atoms form an equilateral triangle. The previous studies[6,8] have reported that the ring minimum is about 1.3 eV above the open minimum. In this paper our calculation also shows that the energy of ring minimum is higher than that of open minimum. According to the above results and experimental evidence,[9] the ground state of ozone should be an open equilibrium structure with C_{2v} symmetry.

Our goal in the present study is to determine a two-dimensional PES for the ozone molecule of point group of C_{2v} in the ground state by using the Sorbie–Murrell many-body expansion potential function, which is simplified by Zhu and Yu[21] by using the symmetry of ozone molecule. Using the PES the height of barrier for the dissociation and recombining of ozone $\{O_3(C_{2v}, \tilde{X}\,^1A_1)\}$, and the O_2–O dissociation energy for ozone in the ground state are calculated. In addition, the *ab initio* calculation of some parameters of ozone in equilibrium is also conducted.

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†Corresponding author. E-mail: shaojx68@163.com

2. Equilibrium parameters in ground state and its dissociation limit

The equilibrium geometries of an ozone in C_{2v} and D_{3h} symmetries are, respectively, optimized using the high-level *ab initio* (i.e. CBS-Q) method,[22] which starts with a zero point energy calculation and a geometry optimization by the Hartree–Fock theory, in which the geometry is further optimized by the second order of Møller–Plesset (MP2) theory. Then the energy is evaluated with MP2 theory with a larger basis set and a CBS extrapolation to correct the energy through the second order MP2. Two additional calculations are used to approximate higher orders of contributions [MP4(SDQ)/6-31+G†† and QCISD(T)/6-31+G†].

Table 1. Equilibrium features of the O_3 in C_{2v} and D_{3h} symmetries, respectively.

	open structure (C_{2v})		ring structure (D_{3h})		
	Cal.	Expt.	Cal.	Theor.[b]	Theor.[c]
R_1/nm	0.12841	0.1275[a]	0.146030	0.14378	0.14367
R_2/nm	0.12841	0.1275	0.146030	0.14378	0.14367
θ/(°)	116.8071	116.75	60.00	60.00	60.00
$E_{\min}$/Hartree	−225.185623	–	−225.139129		
D_e	D_e = 6.2231 eV[d]	6.1656 eV[e]			
Force constant/au $f_{11} = 0.53446$, $f_{12} = 0.03363$, $f_{\theta\theta} = 0.57877$, $f_{1\theta} = 0.09567$ for O_3 (C_{2v})					

[a]Equilibrium bond length and bond angle from Refs.[23,24]. [b]From Ref.[16]. [c]From Ref.[27]. [d]Relative to the dissociation limit $3O(^3P_g)$. [e]From Refs. [25,26].

Using the CBS-Q method, the equilibrium parameters of ozone in C_{2v} symmetry, such as geometry structure parameters, energy, dissociation energy relative to the dissociation limit $3O(^3P_g)$ and force constants, are computed and listed in Table 1. From the Table it is found that the calculated equilibrium geometry structure parameters ($R_1 = R_2 =$ 0.12841 nm, and $\theta = 116.807°$) are in good agreement with those later reported experimental values ($R_1 = R_2 =$0.1275 nm,[23] $\theta = 116.75°$.[24]) In what follows, for the ozone of equilibrium geometry R_1 and R_2 are two bond lengths and θ denotes the angle between them (see, Fig.1). In Table 1 it is seen that the computed dissociation energy for the ozone with C_{2v} symmetry in the ground state has an the absolute error of 0.0575 eV that is in agreement with the experimental value.[25,26]

The equilibrium ring geometry structure of the ozone in D_{3h} symmetry indicated by the CBS-Q calculations is of an equilateral triangle with a bond length of 0.14603 nm, of which the parameters are also listed in Table 1.They are close to the theoretical values from Refs.[16,27]. All other equilibrium parameters of the O_3 with C_{2v} and D_{3h} symmetries, such as energies of the stationary point obtained by the CBS-Q level are listed in Table 1. From the table it is seen that for ozone with an equilibrium geometry, the energy minimum in C_{2v} symmetry is 1.27 eV lower than that of ring structure in D_{3h} symmetry. The similar result is previously reported in Refs.[6,8,9]. As a result, according to the results and experimental evidence,[9] we believe that the ground electronic state of ozone has a C_{2v} equilibrium structure.

The ozone in the ground electronic state has an $^1A_1$ symmetry, and its electronic configuration in C_{2v} symmetry may be described as

$$(1a_1)^2(1b_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(2b_1)^2(5a_1)^2(3b_1)^2 \times (6a_1)^2(1b_2)^2(4b_1)^2(1a_2)^2(2b_2)^\circ.$$

According to the principle of atomic and molecular reaction statics from Ref.[28], when the O_3 molecule with a point group of C_{2v} in its $^1A_1$ ground state dissociates, it may dissociate into O_2 + O in their ground states ($^3\Sigma_g^- + {}^3P_g$) or into O atoms in their ground state (^3P_g), that is

$$O_3(C_{2v}, \tilde{X}^1A_1) \rightarrow \begin{cases} O_2(^3\Sigma_g^-) + O(^3P_g), \\ 3O(^3P_g). \end{cases}$$

3. The potential energy function

An ozone molecule in the ground electronic state may be treated as a molecule having a C_{2v} symmetry. Therefore, the PES is constructed in terms of two bond coordinates, R_1 and R_2, that is, two O–O_1 bond lengths, and a O–O_1–O bond angle θ, where O_1 is a

central atom (see Fig.1).

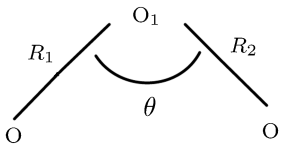


Fig.1. The model of the ozone (C_{2v}, $\tilde{X}\,^1A_1$).

The surface of the ground state $^1A_1$ of ozone in C_{2v} symmetry may be described using a suitable analytical function to provide a smooth continuous variation of the energy with the nuclear coordinates. Therefore, for a triatomic molecule, we can use a Sorbie–Murrell many-body expansion[29] simplified by Zhu and Yu[21] according to the ozone molecule symmetry, i.e. the one that is a sum of one-, two- and tree-body terms:

$$V = \sum V_{\rm A}^{(1)} + \sum V_{\rm AB}^{(2)} + V_{\rm ABC}^{(3)}, \qquad (1)$$

where $V^{(1)}$, $V^{(2)}$ and $V^{(3)}$ denote the one-, two- and three-body terms, respectively. In order to obtain a simple analytical form, we assume the energy of the atom in the ground state [i.e. $O(^3P_g)$] to be zero valued. The one-body term is defined to be zero valued. As a result, the potential energy function of Eq.(1) becomes

$$V = V_{\rm O_1O}^{(2)} + V_{\rm O_1O}^{(2)} + V_{\rm OO}^{(2)} + V_{\rm OO_1O}^{(3)}. \qquad (2)$$

The two-body term, which is a popular function for diatomic system and ever produced the extremely accurate potential energies for 150 diatomic species,[30,31] is determined by using an extended-Rydberg potential up to third order, as follows:

$$V^{(2)} = -D_{\rm e}[1 + \alpha_1\rho + \alpha_2\rho^2 + \alpha_3\rho^3]\exp(-\alpha_1\rho), \quad (3)$$

where $D_{\rm e}$ is the diatomic dissociation energy, and α_1, α_2, and α_3 denote parameters, of which some may be derived from spectroscopic constants or an analytical fit of *ab initio* points. And $\rho = R - R^{\rm e}$, where R and $R^{\rm e}$ are the internuclear separation and they are each equilibrium bond lengths of a diatomic molecule. In this paper α_1, α_2 and α_3 in Table 2 are derived based on the spectroscopic constants (i.e., $\omega_{\rm e}$, $\omega_{\rm e}x_{\rm e}$, $\alpha_{\rm e}$, $B_{\rm e}$ and $D_{\rm e}$) of O_2 in the ground state from Ref.[25].

Table 2. Parameters of potential energy function for O_3 (C_{2v}, $\tilde{X}\,^1A_1$).

two-body term					
species	$D_{\rm e}$/eV	$R_{\rm e}$/nm	α_1/nm^{-1}	α_2/nm^{-2}	α_3/nm^{-3}
O_2	5.14258	0.12075	55.83584	841.56713	6828.58419
tree-body term					
$\gamma_2 = 2.98$	$\gamma_2 = 2.98$				
C_1	262.48002	C_2	317.40095	C_3	50.90545
C_4	−590.85272	C_5	−363.97131	C_6	239.9576
C_7	380.80457				

The three-body term is written as a polynomial P (R_1, R_2, R_3) of the three internuclear separations, multiplied by a range function T (S_1, S_2, S_3) which cancels out the three-body term whenever one atom is moved to infinity from the other two,

$$V^{(3)}(R_1, R_2, R_3) = P(S_1, S_2, S_3) \cdot T(S_1, S_2, S_3),$$

where

$$P(S_1, S_2, S_3) = C_1 + C_2S_1 + C_3S_2^2 + C_4S_3 + C_5S_1S_3 + C_6S_1^2 + C_7S_3^2, \qquad (4)$$

$$T = [1 - \tanh(\gamma_1 S_1/2)][1 - \tanh(\gamma_2 S_2/2)]. \qquad (5)$$

Here γ_1 and γ_2 are the optimization parameters, and $C_i (i = 1-7)$ are the linear parameters, and S_i ($i = 1, 2, 3$) are expressed in terms of displacement coordinates ($\rho_i = R_i - R_i^{\rm e}$) with respect to the ozone in the ground state with a C_{2v} symmetry reference structure (i.e. $R_1^{\rm e} = R_2^{\rm e}$, $R_3^{\rm e}$) as shown below:

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix}.$$

In Table 2, the γ_1 and γ_2 are non-linear parameters that are optimized based on the CBS-Q-computed dissociation energy for removing the oxygen atom out of an ozone molecule $\{O_3(C_{2v}, \tilde{X}\,^1A_1)\}$, i.e. 1.0805 eV, which is in good agreement with the experimental value (1.0494 eV) from Ref.[14].

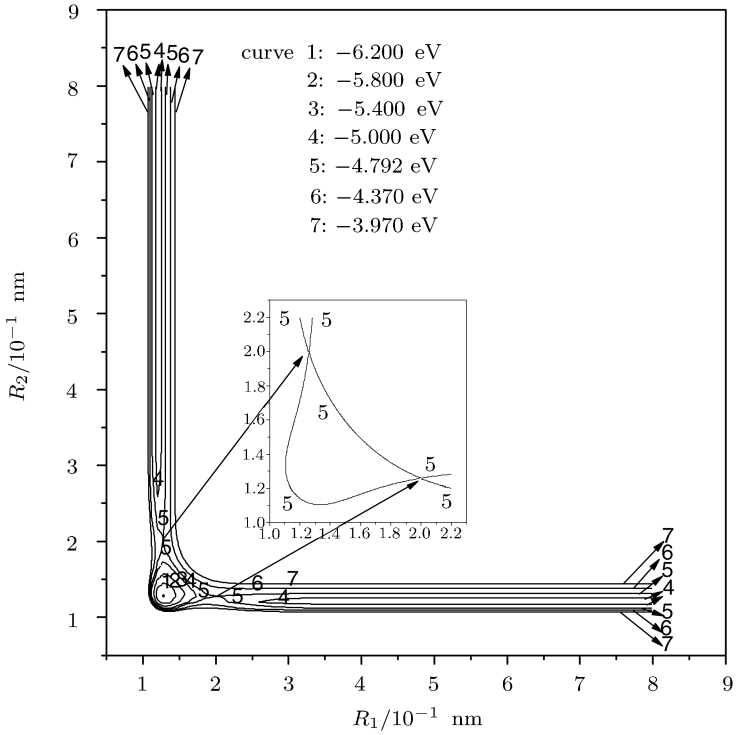


Fig.2. Bond stretching contour of the O_3 surface for a fixed angle of 116.807°.

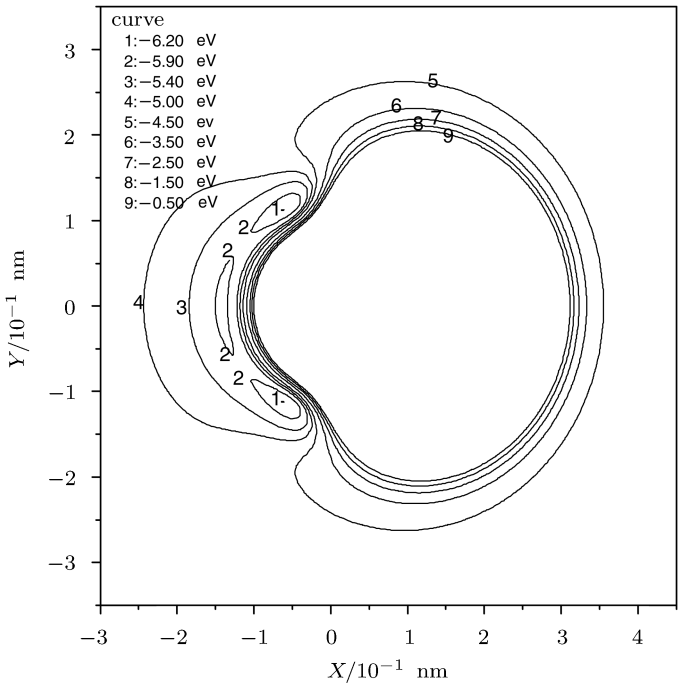


Fig.3. Contour of the O_3 potential for O moving around R_1 (O_1–O), which is fixed at $R_1 = 0.12841$ nm.

Seven linear parameters $C_i (i = 1 - 7)$ are calculated from the equation system including seven independent equations. We know the potential energies, equilibrium geometry parameters (the first derivative of Eq.(2) at equilibrium is zero) and force field (the second derivatives of Eq.(2) evaluated at the minima) for the system of O_3 at equilibrium position. We have seven data, namely seven corresponding indepen-

dent equations, $(V)_e$, $(\partial V/\partial R_1)_e = 0$, $(\partial V/\partial R_3)_e = 0$, $(\partial^2 V/\partial R_1^2)_e = f_{11}$, $(\partial^2 V/\partial R_1 \partial R_2)_e = f_{12}$, $(\partial^2 V/\partial \theta^2)_e = f_{\theta\theta}$, $(\partial^2 V/\partial R_1 \partial \theta)_e = f_{1\theta}$, where the subscript e refers to the evaluation at the equilibrium position and f_{11}, f_{12}, $f_{\theta\theta}$ and $f_{1\theta}$ are the computed force constants for O_3 (see, Table 1). These data are sufficient to determine the seven linear parameters.

The other computed parameters of the ozone potential energy function, such as two-body term parameters, are summarized in Table 2. The contours of the PES for ozone in the ground state (C_{2v}, $\tilde{X}\,^1A_1$) according to the potential energy function (Eq.(2)), are depicted in Figs.2 and 3.

4. Results and discussion

Contours of the PES for O_3 (C_{2v}, $\tilde{X}\,^1A_1$) with the potential energy function (Eq.(2)) are depicted in Figs.2 and 3, and they clearly display the structure feature of O_3 in the ground state. In a channel, barrier is a crucial parameter, and its existence and magnitude have an important effect on the property of kinetics. From Fig.2, a bond stretching contour of the O_3 surface shows that there is a saddle point in this dissociation channel at $\theta = 116.807°$, with $R_1 = 0.19990$ nm and $R_2 = 0.12547$ nm, and with a barrier being 1.4311 eV for the dissociation process of ozone in the ground state. A similar feature was reported in Ref.[14]. The barrier for the dissociation process of ozone was measured to be 0.98496 eV[32] when a catalyzer was used, so the measured value of barrier (1.4311 eV) for the dissociation process without using any catalyzer should be reasonable. In addition, from Fig.2, we obtain a barrier of 0.3236 V for the $O_2(^3\Sigma_g^-)$ + O (^3P) recombination, which is consistent with the calculation result (see the figure) in Ref.[12], and similar conclusions were also reported in Refs.[33–35].

In Fig.3, a contour of the O_3 potential for O moving around R_1, which is fixed at R_1 (O_1–O) = 0.12841 nm on the x-axis (O_1, central atom, is located at a coordinate origin), clearly indicates the equilibrium structure feature of O_3 (C_{2v}, $\tilde{X}\,^1A_1$) and has a saddle point. The figure is helpful to the experimental analysis and application of cross molecular beam to ozone.

Owing to the notorious difficulty in calculating the electronic structure of ozone, even in the lowest state, the construction of an accurate PES is a formidable task.[8] However, with the Sorbie–Murrell many-body expansion potential function we may depict the satisfactory PES of ozone in the ground state, which is able to yield the reliable crucial parameter and barrier. The PES of $O_3(\tilde{X}\,^1A_1)$ will be used for investigating the detailed dynamics in several directions, for example, quantal and classical dissociation dynamics for a non-rotating or a rotating $O_3(\tilde{X}\,^1A_1)$, quantal and classical bimolecular reaction dynamics for different isotopomers in order to evaluate the consequence of reducing the symmetry. Eventually it might become possible to explain the observed unusually high enrichment in some of the isotopomers as well as the peculiar temperature- and pressure- dependent recombination rates through the rigorous dynamics calculation of one (or possibly several) potential energy surface(s).

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