

Ab initio theoretical calculation and potential energy surface for ground-state HO₃

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Abstract

The potential energy surface for the HO₃ → HO + O₂ reaction has been studied using the QCISD(T)/CBS (complete basis set) method. The HO₃ molecule is found to be stable relative to the HO + O₂ dissociation limit. It has a planar equilibrium geometry, with the *cis*-HO₃ structure being slightly more stable than the *trans*-HO₃ one. The classical dissociation barrier height is predicted to be 8.87 kcal mol⁻¹. Based on the calculated energy points, a new double many-body expansion (DMBE II) potential energy surface for HO₃ was obtained. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrogen trioxide HO₃ has long been assumed to be an important intermediate in atmospheric and combustion chemistry [1]. In the past decades, due to lack of direct experimental evidence, the problem of stability of the HO₃ species has received numerous theoretical investigations [2–11]. However, the calculated results give contradictory answers. Although Dupuis et al. [6] predict HO₃ to be stable relative to the HO + O₂ dissociation limit from the MC(DZP) method, most high level theoretical calculations [4,7,10] suggest such a species to be metastable. Recently, the stability problem has been solved by two experimental measure-

ments [1,12]. The Fourier-transform ion cyclotron resonance mass spectrometry [12] study shows that the HO₃ molecule is relatively stable by 10 ± 5 kcal mol⁻¹ with respect to HO + O₂. In turn, Cacace et al. [1] detected directly a stable HO₃ molecule using neutralization–reionization and neutralization–reionization/collisionally activated dissociation mass spectrometry. This work has also indicated that HO₃ has a H–O–O–O connectivity.

There is a global single-valued double many-body expansion (denoted as DMBE I) potential energy surface for ground-state HO₃ [10], which was modelled using UCISD ab initio calculations as calibrating data. Such a surface predicts a metastable HO₃ structure. Thus, to conform with the above-mentioned experimental results, it seems imperative to obtain a more accurate potential energy surface. However, in spite of such a limitation, the DMBE I potential energy surface has been successfully employed to study the dynamics of both the H + O₃ [13,14] and O + HO₂ [15,16]

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reactions. In fact, the thermal rate constants calculated from the DMBE I potential energy surface are found to be in good agreement with the available experimental measurements. Since both reactions are very exoergic, it appears that the small well depth of the HO₃ intermediate can hardly affect the involved kinetic properties except perhaps for the rotational and vibrational energy distributions of the reaction products [13]. The reported dynamics results also show that the DMBE I potential energy surface describes well the H + O₃ and O + HO₂ entrance channels. However, the HO₃ intermediate species can play a more crucial role in the reverse HO + O₂ collisional process [17,18], which provided a strong motivation to carry out the current investigation.

In this Letter, we use a high level ab initio method, QCISD(T)/CBS, to study the potential energy surface for the HO₃ → HO + O₂ reaction. Then, by using the energy switching [19] method, a new DMBE potential energy surface (referred to as double many-body expansion (DMBE II)) is constructed by merging an extra four-body energy term which fits the calculated QCISD(T)/CBS energy points with the original DMBE I potential energy surface.

2. Ab initio calculations for the reaction HO₃→HO + O₂

It is very challenging to calculate an accurate potential energy surface due to the incomplete treatment of the correlation energy which results both from the CI truncation and the basis set superposition error. Often, the latter is the largest source of error to the correlation energy. Thus, in order to obtain a chemically accurate potential energy surface, very large basis sets are usually required. However, such basis sets pose a formidable task for HO₃ if one has to calculate several thousand energy points as it contains three oxygen atoms. In this work, rather than using a large basis set, we will employ an extrapolation scheme due to Halkier et al. [20] which allows to estimate the basis set superposition error. Such a scheme has been claimed to significantly improve the accuracy of the calculated results, leading typically to errors

of a few (often 1 or 2) kcal mol⁻¹; for a recent review, see Ref. [21].

The basis set errors are corrected in the Møller-Plesset second-order (MP2) perturbation theory [20] by using

$$E_{\text{MP2}}(X) \approx E_{\text{MP2}}(\infty) + aX^{-3}, \quad (1)$$

where $E_{\text{MP2}}(X)$ and $E_{\text{MP2}}(\infty)$ are the MP2 energies calculated at the cc-pVXZ [22] basis set and complete basis set limits, respectively, X is the cardinal number which identifies the basis set used, and a is a parameter to be determined. If cc-pVDZ ($X = 2$) and cc-pVTZ ($X = 3$) basis sets are then utilized, the MP2 energy assumes the form

$$E_{\text{MP2}}(\infty) = \frac{27}{19}E_{\text{MP2/cc-pVTZ}} - \frac{8}{19}E_{\text{MP2/cc-pVDZ}}, \quad (2)$$

while the cc-pVDZ basis set error correction is given by

$$\begin{aligned} \Delta E_{\text{bs}} &= E_{\text{MP2}}(\infty) - E_{\text{MP2/cc-pVDZ}} \\ &= \frac{27}{19}(E_{\text{MP2/cc-pVTZ}} - E_{\text{MP2/cc-pVDZ}}). \end{aligned} \quad (3)$$

Assuming now that the basis set error does not vary significantly with the level of theory, the QCISD(T)/CBS energy can be obtained as

$$\begin{aligned} E_{\text{QCISD(T)/CBS}} &= E_{\text{QCISD(T)/cc-pVDZ}} \\ &+ \frac{27}{19}(E_{\text{MP2/cc-pVTZ}} - E_{\text{MP2/cc-pVDZ}}). \end{aligned} \quad (4)$$

This equation will be used in the ab initio calculations reported in the present work. As the MP2/cc-pVDZ energy can be produced during the QCISD(T)/cc-pVDZ calculation, one needs only to carry out an extra calculation using the MP2/cc-pVTZ method to obtain the QCISD(T)/CBS energy. All calculations have been carried out using the GAUSSIAN 94 computer code [23].

A total of 5038 energy points have been computed, distributed mainly over the interaction potential region and the HO + O₂ asymptotic channel. From these energies, we have found three stationary points using a local harmonic fitting procedure. The results obtained are gathered in Table 1. It is seen that there are two stable planar HO₃ isomers, with the *cis*-HO₃ species being more

Table 1

Geometries and energies for *cis*-HO₃ and *trans*-HO₃ minima, and HO⋯O₂ transition state (TS), calculated from the QCISD(T)/CBS method, where Δ*E* denotes the energy difference relative to the HO + O₂ asymptote

	<i>Cis</i> -HO ₃	<i>Trans</i> -HO ₃	HO⋯O ₂ (TS)	HO + O ₂
<i>R</i> _{HO_x} (<i>a</i> ₀)	1.8299	1.8299	1.8298	1.8298
<i>R</i> _{O_aO_b} (<i>a</i> ₀)	2.7723	2.8245	3.5683	
<i>R</i> _{O_bO_c} (<i>a</i> ₀)	2.3376	2.3691	2.3055	2.2820
θ _{HO_xO_b} (deg)	95.60	95.76	96.40	
θ _{O_aO_bO_c} (deg)	110.01	110.0	110.39	
φ _{HO_xO_bO_c} (deg)	0.0	180.0	113.10	
<i>E</i> (<i>E</i> _h)	-225.859039	-225.857201	-225.844894	-225.848694
Δ <i>E</i> (kcal mol ⁻¹)	-6.49	-5.34	2.38	0.0

stable than the *trans*-HO₃ one. They are 6.49 and 5.34 kcal mol⁻¹ lower than the HO + O₂ dissociation limit, respectively. These values are comparable with the experimental estimate of 10 ± 5 kcal mol⁻¹ [12]. Note that the theoretical values represent absolute energies without zero-point energy corrections. Although the coplanar equilibrium geometry of the HO₃ molecule differs somewhat from previous results [2,3,6,10], it is consistent with the most recent CASPT findings of Setokuchi et al. [11] who reported these stable isomers. However, they predict the *trans*-HO₃ structure to be more stable than the *cis*-HO₃ one. Yet, as they also discuss [11], the relative stability between the *cis*-HO₃ and *trans*-HO₃ structures as well as the central O–O bond length are very sensitive to the method used. We believe that the QCISD(T)/CBS method reported in the present work may have led to an improved accuracy in the final results. Our calculations also led to a prediction of a non-planar HO⋯O₂ transition state, which is found to lie 2.38 kcal mol⁻¹ higher than the HO + O₂ dissociation limit. Finally, all stationary structures show a longer central O–O bond in comparison to the terminal one.

3. Potential energy surface

The single-valued DMBE II potential energy surface for HO₃ is written as [19,24]

$$V_{\text{II}} = V_{\text{I}} + \sum_I V_I + f(E)V_{\text{EHF2}}^{(4)}, \quad (5)$$

where the new four-body Hartree-Fock term assumes the form

$$V_{\text{EHF2}}^{(4)} = P_2^{(4)} T_2^{(4)} \quad (6)$$

and *V*_I is the DMBE I potential energy surface [10]. Moreover, *V*_I is a local Gaussian function defined by

$$V_I = A_l^g \sum_{\beta\gamma} e^{-\sum_{i=1}^6 \eta_i \rho_i^2(A\alpha\beta\gamma)}, \quad (7)$$

where the variables are defined, for the configuration (*Aαβγ*), as

$$\rho_1 = R_{Ax} - R_{Ax}^0, \quad (8)$$

$$\rho_2 = R_{x\beta} + R_{x\gamma} - R_{\beta\gamma}^0, \quad (9)$$

$$\rho_3 = R_{x\beta} - R_{x\gamma}, \quad (10)$$

$$\rho_4 = \cos \theta_{Ax\beta} + \cos \theta_{Ax\gamma} - \cos \theta_x^0, \quad (11)$$

$$\rho_5 = \cos \theta_{A\alpha\beta} - \cos \theta_{A\alpha\gamma}, \quad (12)$$

$$\rho_6 = \cos \theta_{\beta x\gamma} - \cos \theta_{\beta\gamma}^0, \quad (13)$$

θ_{*ijk*} are the bond angles, and (*R*_{*Aα*}⁰, *R*_{*βγ*}⁰, θ_{*x*}⁰, θ_{*βγ*}⁰) is a set of reference bond distances and bond angles. The addition of such local terms *V*_I was found necessary to eliminate spurious unphysical minima during the fitting procedure. As in DMBE I, *A* and (*αβγ*) stand for the hydrogen and oxygen atoms.

In turn, *f*(*E*) in Eq. (5) is the energy switching function used to cancel out the contribution of the four-body energy term *V*_{EHF2}⁽⁴⁾ at all asymptotic channels but OH + O₂. Such an energy switching function is typically a hyperbolic tangent function [19]. We emphasize that the dynamics calculations carried out for the H + O₃ and O + HO₂ reactions have shown that the DMBE I potential energy surface quantitatively describes these reactant channels, which have therefore been kept unchanged.

The range function and fourth-order polynomial in $V_{\text{EHF2}}^{(4)}$ have been written as

$$T_2^{(4)} = \{1 - \tanh(\gamma_1 S_1/2)\}\{1 - \tanh(\gamma_2 S_4/2)\}, \quad (14)$$

$$P_2^{(4)} = \sum_{i,j,k,p} a_{i,j,k,p} S_1^i S_4^j \prod_{p=1}^8 t_p^{k_p}, \quad (15)$$

where S_1, S_4 and

$$t_p = \{S_2^2 + S_3^2, S_5^2 + S_6^2, S_2 S_5 + S_3 S_6, S_3^3 - 3S_3 S_2^2, S_6^3 - 3S_6 S_5^2, S_6(S_3^2 - S_2^2) - 2S_2 S_3 S_5, S_3(S_6^2 - S_5^2) - 2S_2 S_5 S_6, (S_3 + S_6)^3 - 3(S_3 + S_6)(S_2 + S_5)^2\}.$$

These are the 10 totally symmetric integrity functions given in Ref. [10], which are invariant under permutation operation of any two equivalent oxygen atoms of HO_3 . Consequently, the HO_3 potential energy surface is totally symmetric under permutation of any two oxygen atoms of HO_3 . Note that S_i are the symmetric coordinates defined in Ref. [10] but using a different set of reference geometries.

The parameters in Eqs. (14) and (15) were fitted to the 5038 ab initio points, which essentially distribute over the potential region describing the dissociation process $\text{HO}_3 \rightarrow \text{HO} + \text{O}_2$. Such points span an energy range of $0.051 E_h$ ($32.0 \text{ kcal mol}^{-1}$). A non-linear least-squares fitting method was used together with a Monte-Carlo technique for the non-linear variables. The fitted surface shows a root-mean-square error of $1.2 mE_h$ ($0.75 \text{ kcal mol}^{-1}$) with a maximum error of $2.6 mE_h$. We emphasize that the deviations along the *cis*- HO_3 and *trans*- HO_3 minima, and transition state $\text{HO} \cdots \text{O}_2$, are even smaller since large weights have been assigned to the involved points during the least-squares fitting procedure. In other words, the fitting error is roughly within the error of the ab initio calculations. As the new potential energy surface involves 158 extra parameters, they will not be given here; they can be obtained upon request by e-mail (varandas@qtvsl.qui.uc.pt) from the authors.

The new DMBE II potential energy surface essentially gives the same properties as DMBE I [10] for the $\text{H} + \text{O}_3$ and $\text{O} + \text{HO}_2$ channels due to the use of the energy switching function in Eq. (5). For instance, Fig. 1 shows the energy plot for an

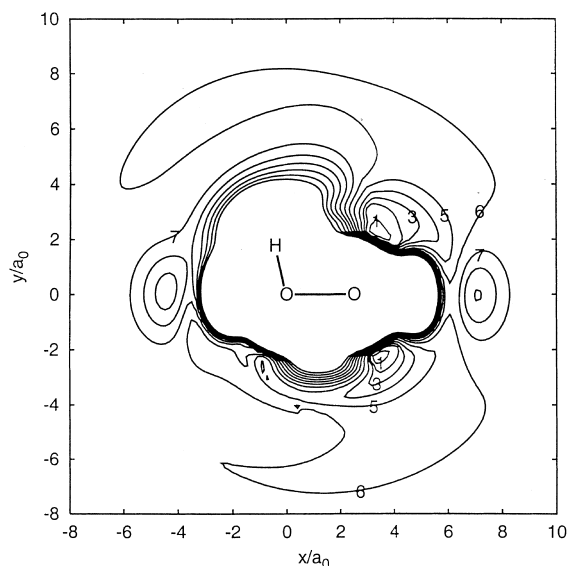


Fig. 1. Contour plot for an oxygen atom moving coplanarly around a HO_2 molecule, where $R_{\text{HO}} = 1.8431 a_0$ and $\theta_{\text{HOO}} = 104.8^\circ$ are fixed and the O–O bond length is partially relaxed from 2.28 to $2.58 a_0$. The contours start at $-0.355 E_h$ and are equally spaced by $0.015 E_h$.

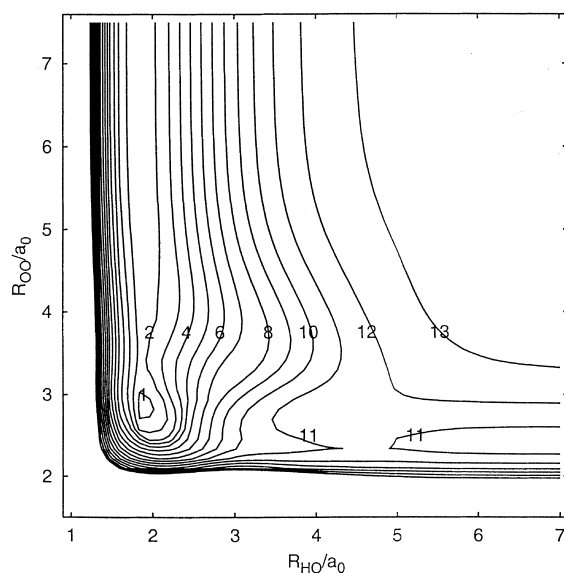


Fig. 2. Contour plot for the $\text{H} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2$ reaction at a given torsion angle of $\phi_{\text{HO}_2\text{O}_2} = 90.0^\circ$ and bond angle $\theta_{\text{HO}_2\text{O}_2} = 95.60^\circ$, with the unbroken O–O bond ($2.26 a_0 \leq R_{\text{O}_2\text{O}_2} \leq 2.42 a_0$) and the bond angle $\theta_{\text{O}_2\text{O}_2\text{O}_2}$ (106.0° – 121.0°) being partially relaxed. The contours start at $-0.368 E_h$ and are equally spaced by $0.014 E_h$.

oxygen atom moving coplanarly around a partially relaxed HO₂ molecule. Both *cis*-HO₃ and *trans*-HO₃ minima are clearly visible. Note that there is no classical barrier for their formation from O + HO₂. Therefore, for the O + HO₂ reaction, the long-range interaction potential can play an important role in the involved dynamics [15,16].

On the other hand, the DMBE II potential energy surface significantly improves the accuracy to describe the HO₃ → HO + O₂ reaction and the reverse process. Fig. 2 shows a contour plot for the H + O₃ → HO + O₂ reaction. Visible are the saddle points located in the entrance and exit chan-

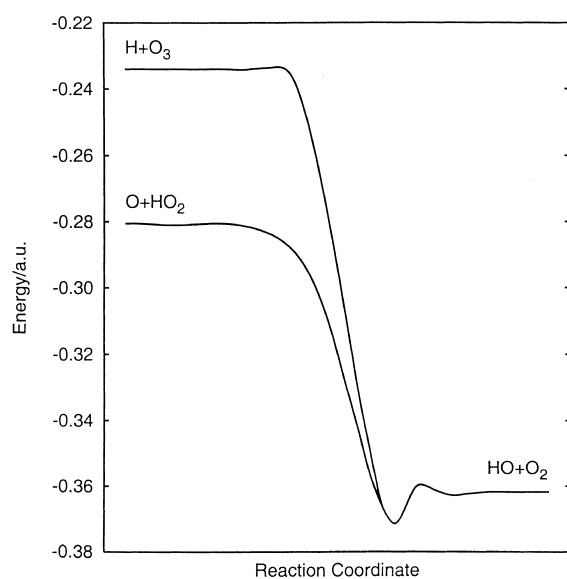


Fig. 3. Minimum energy paths for the H + O₃ → HO + O₂ and O + HO₂ → HO + O₂ reactions obtained from the HO₃ DMBE II potential energy surface.

nels. Also seen is the minimum associated to HO₃, which is a stable species relative to the HO + O₂ asymptote. These features are collectively represented by the minimum energy paths for the H + O₃ → HO + O₂ and O + HO₂ → HO + O₂ reactions shown in Fig. 3.

The stationary points calculated from the DMBE II potential energy surface for the H + O₃ → HO + O₂ reaction are given in Table 2. As indicated, there are two stable planar HO₃ structures, whose energies lie below the HO + O₂ dissociation limit: the *cis*-HO₃ structure is more stable than the *trans*-HO₃ one, although the energy difference is only 1.35 kcal mol⁻¹. Clearly, their geometries and relative energy are in good agreement with the QCISD(T)/CBS results (see Table 1). The *cis*-HO₃ molecule has a classical barrier height of 7.84 kcal mol⁻¹ to dissociate and form HO + O₂. Compared to the ab initio value of 8.87 kcal mol⁻¹, the barrier height is only about 1.0 kcal mol⁻¹ lower. A more subtle difference refers to the fact that the transition state determined from the DMBE II potential energy surface has a planar *cis*-HO₃ structure. This is not expected to be a major problem as the torsion normal mode frequency of the transition state is very small, i.e., 83 cm⁻¹.

4. Conclusions

The QCISD(T)/CBS method has been used to study the potential energy surface for the HO₃ → HO + O₂ reaction. Two stable HO₃ isomers were obtained: both have a planar structure, with the *cis*-HO₃ species being more stable than

Table 2

Geometries and energies for *cis*-HO₃ and *trans*-HO₃ minima, HO...O₂ transition state (TS), and van der Waals complex for the HO₃ → HO + O₂ reaction calculated from the DMBE potential energy surface

	<i>Cis</i> -HO ₃	<i>Trans</i> -HO ₃	HO...O ₂ (TS)	HO...O ₂ (complex)	HO + O ₂
R_{HO_2} (a ₀)	1.8468	1.8201	1.8119	1.8360	1.8344
$R_{\text{O}_a\text{O}_b}$ (a ₀)	2.7914	2.7976	3.4927	6.9637	
$R_{\text{O}_b\text{O}_c}$ (a ₀)	2.3793	2.3555	2.3069	2.2830	2.2818
$\theta_{\text{HO}_a\text{O}_b}$ (deg)	97.69	101.01	98.78	172.03	
$\theta_{\text{O}_a\text{O}_b\text{O}_c}$ (deg)	110.24	109.87	125.37	80.32	
$\phi_{\text{HO}_a\text{O}_b\text{O}_c}$ (deg)	0.0	180.0	0.0	180.0	
V (E _h)	-0.372105	-0.369958	-0.359605	-0.362727	-0.361777

the *trans*-HO₃ one. The energy of *cis*-HO₃ is lower by 6.49 kcal mol⁻¹ than the HO + O₂ one. Its classical dissociation barrier height was predicted to be 8.87 kcal mol⁻¹. Moreover, a single-valued double many-body expansion (DMBE II) potential energy surface has been obtained by fitting the 5038 QCISD(T)/CBS energy points to a suitable functional form which was then combined with the DMBE I surface by using the energy switching [19] method. The new DMBE II surface gives a root-mean-square error of 0.75 kcal mol⁻¹. Its major attributes are in good agreement with the ab initio calculations.

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