

REVIEW

Quantum Dynamics of Oxyhydrogen Complex-Forming Reactions for the HO₂ and HO₃ Systems

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Complex-forming reactions widely exist in gas-phase chemical reactions. Various complex-forming bimolecular reactions have been investigated and interesting phenomena have been discovered. The complex-forming reactions usually have small or no barrier in the entrance channel, which leads to obvious differences in kinetic and dynamic characteristics compared with direct reactions. Theoretically, quantum state-resolved reaction dynamics can provide the most detailed microscopic dynamic mechanisms and is now feasible for a direct reaction with only one potential barrier. However, it is of great challenge to construct accurate potential energy surfaces and perform accurate quantum dynamics calculations for a complex polyatomic reaction involving deep potential wells and multi-channels. This paper reviews the most recent progress in two prototypical oxyhydrogen complex-forming reaction systems, HO₂ and HO₃, which are significant in combustion, atmospheric, and interstellar chemistry. We will present a brief survey of both computational and experimental work and emphasize on some unsolved problems existing in these systems.

Key words: Complex-forming reaction, Potential energy surface, Reaction kinetics, Quantum dynamics

I. INTRODUCTION

Molecular reaction dynamics, which focuses on the fundamental law and nature of the chemical reaction at the level of atom and molecule, is one of the most important branches of theoretical and computational chemistry. Due to the quantum mechanical nature of the motion of electron and nucleus, only quantum treatments can provide the definitive characterisation of the reaction dynamics. The quantum dynamical theories have achieved great success during the past 40 years [1–11] since the first quantum state-resolved dynamical calculation for the simplest H+H₂ system was carried out [1]. Quantum state-resolved dynamical study can provide the most detailed microscopic mechanism for chemical reactions and has become a major tool for understanding the multi-dimensional dynamics, tunneling, isotopic effect, mode selectivity, nonadiabatic effect, and reaction resonance state. The close collaboration between theory and experiment has uncovered some important dynamical characteristics for many important elementary reactions, such as F+H₂/HD [6, 8, 12], Cl+H₂/HD [10, 13], and HD+OH [14].

Bimolecular reactions accompanied by the formation of reaction intermediates have attracted much attention

due to their crucial role in combustion, atmosphere, and interstellar media. These reactions are usually barrierless in the entrance channel and involve at least one potential well along the reaction path, which are called as complex-forming reactions. The kinetic and dynamic characteristics of complex-forming reactions are much different from those in direct reaction which has only one potential barrier. Experiments can provide a lot of valuable information but cannot present very clear and complete understanding of the detailed microscopic mechanism for these reactions. So, the accurate theoretical studies are highly demanded. Both quasi classical trajectory (QCT) and quantum dynamic methods can provide detailed information on reaction dynamics, such as cross sections, product state distributions, and rate constants. The QCT method is less expensive but cannot describe the quantum effects correctly. Accurate quantum dynamical calculations for complex-forming reaction are still difficult, because of the large basises or grids required for converged quantum description in potential well(s) and long-range electrostatic interaction range [15].

The reactions O+HO₂→HO+O₂ and O+OH→H+O₂ are elementary reaction processes that govern HO_x radical concentration in the upper stratosphere [16] and mesosphere [17, 18] and play significant roles in the cycle for ozone depletion. The O+HO₂ is also a chain-breaking step in combustion processes. Substantial experimental and theoretical interest have been at-

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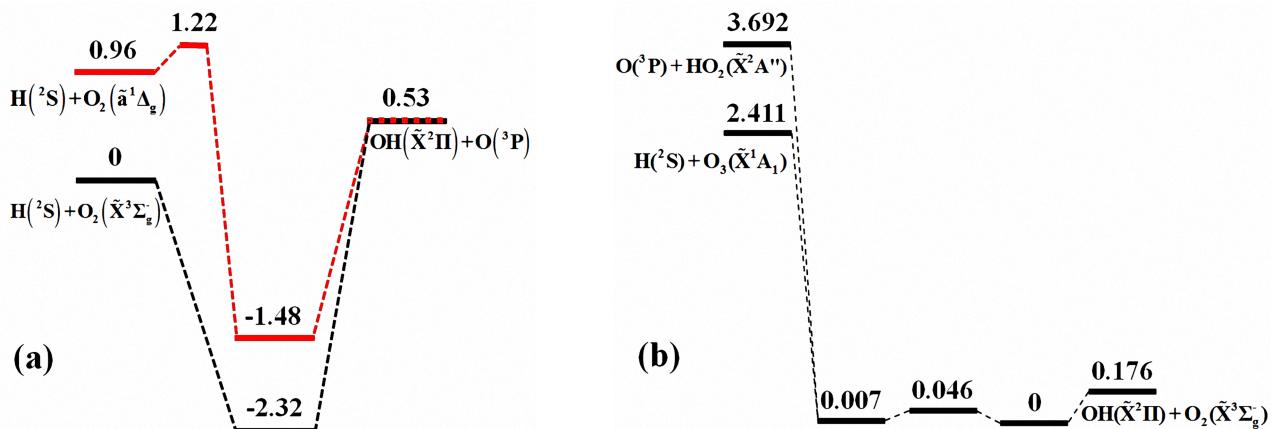


FIG. 1 Schematic illustration of the reaction pathways for (a) HO_2 and (b) HO_3 reaction systems. The energies are taken from the results of Li *et al.* [92] in eV relative to the ground state reactant asymptotes for HO_2 and the results from the calculations by using MRCI-F12 method with VDZ-F12 basis in eV relative to the global minimum for HO_3 , respectively.

tracted focusing on the kinetic and dynamic characteristics of these reactions. However, HO_2 and HO_3 are still regarded as dynamically “elusive”, presenting as yet unresolved challenges for rigorous quantum theoretical treatment. In this review, we give a detailed presentation in the advance of kinetic and dynamic investigations of these complex-forming reactions and attempt to reveal some potential characteristics of complex-forming reaction.

II. THE HO_2 SYSTEM

The endothermic reaction between hydrogen atom (H) and oxygen molecule (O_2)



is long known as the most important combustion reaction [19] because of its crucial role in chain breaking of hydrogen oxidation and molecular oxygen consuming step. Such reaction also represents an important prototype complex-forming reaction with deep well (2.32 eV, as shown in FIG. 1(a)). The reverse reaction between $\text{OH}({}^2\tilde{\Pi})$ and $\text{O}({}^3\text{P})$ also plays an important role in atmospheric chemistry [17] as well as in interstellar chemistry [20].

To understand the mechanism of such reactions, considerable attentions have been attracted in theoretical studies on the adiabatic potential energy surface (PES). Since Melius and Blint [21] constructed the first analytic PES (MB PES) of the system in 1979, PES for the ground electronic state (${}^2\tilde{\text{A}}''$) of HO_2 has been developed by several groups at different *ab initio* levels of theory. Earlier PESs include the double many-body expansion (DMBE) IV PES [22] which combined *ab initio* and experimental data simultaneously, the diatomics-in-molecules (DIM) surface [23] which utilized the diatomics in molecules model to fit *ab initio* data, and

an analytical representation [24] (TU PES) of an *ab initio* potential focusing on the minimum energy path (MEP) and the anisotropies in its vicinity. Among the aforementioned PESs, DMBE IV PES is probably the most popular and widely used in dynamical studies for the reasonable behavior in describing global properties of the reaction. Besides, several deficiencies of the semi-empirical PES have been reported [24–30], which may significantly affect the accuracy of kinetics. For instance, the reaction was suggested to process a direct reaction channel by the dynamic study on the DMBE IV PES [27], which conflicts with the experimental complex-forming mechanism. To better understand the vibrational spectrum and dynamics of the system, Xu *et al.* [31, 32] recently calculated about 18000 *ab initio* points using multi-reference configuration interaction method with Davidson correction and an augmented quadruple zeta correlation consistent basis set (MRCI+Q/AVQZ). They constructed a new global PES (XXZLG PES) of $\text{HO}_2({}^2\tilde{\text{A}}'')$ by three-dimensional cubic spline interpolation.

Due to the nature of complex-forming reaction with a deep well, most theoretical dynamics studies of $\text{H} + \text{O}_2({}^3\tilde{\Sigma}_{\text{g}}^-)$ reaction have been carried out by using QCT [33–39] or statistical models [31, 40–43]. Serious deficiencies have been pointed out, despite some reasonable results have been obtained by the heroic efforts. Dynamic bottleneck in energy transfer of the system [15] was proposed due to the observations of many back trajectories violating zero point energy (ZPE) of the OH product [35] and non-statistical limit of the $\text{H} + \text{O}_2$ reaction [37]. The statistical approach was found to reproduce only a few total reaction probabilities and led to serious discrepancies with exact total reactive integral cross-sections (ICS) [42–44]. Several observations have confirmed that the $\text{H} + \text{O}_2$ reaction is not completely statistical [39, 44–46]. The dynamics of the reverse $\text{OH} + \text{O}$ reaction are also extensively investigated utilizing QCT

method [22, 24, 38, 47–54]. Like in the H+O₂ reaction, it is also not completely perfect when QCT approach was used in treating the dynamics of the OH+O reaction and dynamic bottleneck still exists in spite of using different PESs [36–38]. Therefore, a quantum treatment is very necessary. It is still a controversial issue that whether or not the OH+O reaction is statistical. The significant non-reactive scattering was found in earlier QCT studies [22, 38, 47–50], implying that the reaction has a non-statistical component, while latter work revealed that the non-statistical channel is unimportant [24]. Some evidences have manifested that the origin of the non-statistical behavior could be attributed to the relative short living HO₂ complex and the inefficient intramolecular vibrational energy redistribution (IVR) [29, 30, 43, 44, 54, 55].

The quantum mechanical characterization of the HO₂ system has been reported by many groups on various PESs since the end of last century. The $J=0$ total reaction probability was reported by Pack *et al.* [56, 57] using time-independent quantum mechanical (TIQM) method on DMBE PES at several collision energies and a threshold was found, which is consistent with the endothermicity of the H+O₂ reaction. It was confirmed later by quantum dynamical studies [55, 58, 59]. Numerous sharp resonances were shown in total reaction probability [55, 58–61], revealing the complex-forming mechanism. TIQM calculations on H+O₂ reaction are extended to total angular momentum $J>0$ and Coriolis coupling was explicitly included [27, 62–64], which revealed that the importance of Coriolis coupling increases with J increasing. Due to its extensive Coriolis coupling, HO₂ system served as a rigorous benchmark for helicity conserving method and J -shifting models [65–68]. Poirier *et al.* [69–71] addressed approximated quantum dynamics calculations on the HO₂ bound rovibrational state using various theory-based J -shifting schemes. They found that the rovibrational energy levels were extremely well performed even up to large J values where Coriolis coupling cannot be ignored by so-called “modified Effective Potential” (modEP) method [71].

The XXZLG PES has been widely used in quantum dynamical studies. Both time-dependent quantum mechanical (TDQM) and TIQM methods were used to calculate the total and state-to-state quantum mechanical reaction probability. Remarkably dynamic difference was found, comparing with the results on DMBE PES, especially at collision energies larger than 1.2 eV [59]. The reactivity of the H+O₂ reaction was significantly enhanced by the effect of the vibrational excitation [72], as expected in terms of the Polanyi rule [73]. The initial rotational excitation on the O₂ reactant was later carried out by using Chebyshev wave packet calculations and the higher rotational states of O₂ seem to bring better agreement with experiments [74]. The quantum rate constants [72, 74] were found to be significantly improved on the XXZLG PES com-

pared with those obtained on the DMBE PES, and the temperature dependence of Arrhenius type was reasonably produced. Even though, the calculated values still underestimated compared with the experimental values and the influence factors were not ascertained. Regarding to the reaction, the quantum rate constants [75] on the XXZLG PES were qualitatively consistent with a low-temperature extrapolation of earlier experimental values but smaller than the most recent experiments at the lowest temperatures reported by Carty *et al.* [45], which may stem from the particularly vulnerable region of the channel with difficulty in the long-range interaction fitted by splines [32, 76, 77]. It has been demonstrated [15, 78, 79] that the long-range force plays an important role at low-temperature. Two reproducing kernel Hilbert space (RKHS) PESS [80] were designed in order to better elucidate the dynamics and accurately describe the potential well corresponding to the bound state of HO₂.

To remedy the deficiencies in the fitting, especially at long-range interaction region, of XXZLG PES, Varandas *et al.* [81] have very recently developed a new PES for HO₂(\tilde{X}^2A''), commonly known as Combined-Hyperbolic-Inverse-Power-Representation (CHIPR) PES, which employed the slightly corrected *ab initio* data of Xu *et al.* [32] using the novel Varandas CHIPR method [82]. The main topographical features of CHIPR PES are in good agreement with XXZLG PES, as shown in FIG. 2. However, some differences in long-range region, such as the undulations visible of XXZLG PES, may lead to distinguished behavior in the OH+O dynamics. Rate constants calculated by QCT method on this new PES are in general agreement with the XXZLG results from moderate temperatures upwards, but the disparity can be up to 25% at low temperatures [81]. It is thus confirmed that long-range forces in the barrierless OH+O reaction could dominate the rate constants [83, 84]. Time-independent quantum scattering calculations have been performed on the CHIPR PES and thermal rate coefficients are reported, as shown in FIG. 3, by using the J -shifting approximation [85]. It is a remarkable fact that the most recent experimental values of Carty *et al.* [45] showed a distinct trend from other early experiments but close to the calculated ones. The quantum rate constants considering the influence of quantum effects in the intermediate complex were somewhat larger than the QCT results [81], although a similar pattern was reproduced. Meanwhile, the hydrogen isotopic substitution X+O₂→OX+O (X=Mu, H, D and T) reactions were performed by employing time-independent method and the effect of isotopic substitution on state specified rate constants was investigated [86]. Rate constants of the reactions with H, D, and T presented quite similar behavior while the Mu+O₂ rate constants were smaller than others over the entire temperature range, especially at low temperature. Reaction probabilities for different initial rovibrational states of the OH radical

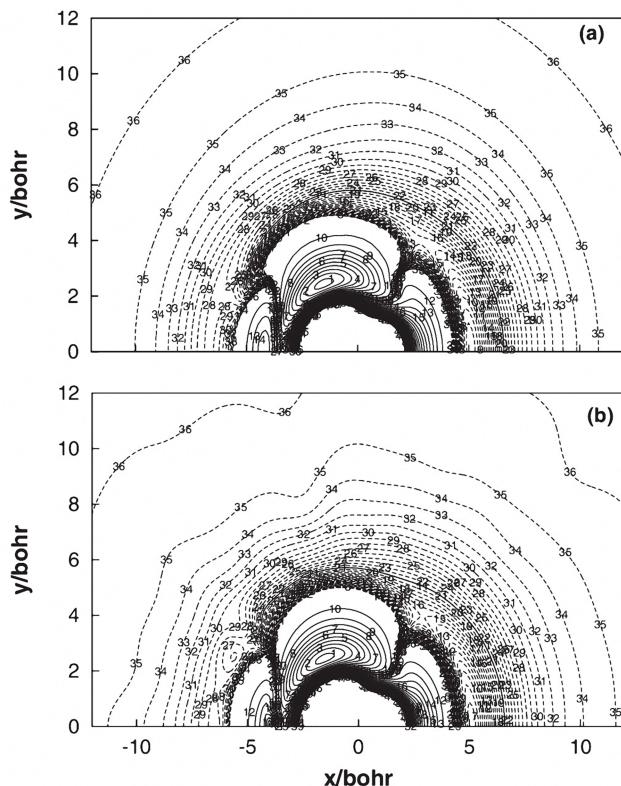
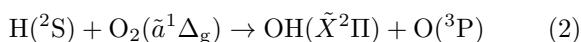


FIG. 2 Topographical features of CHIPR (a) and XXZLG (b) PESs for an oxygen atom moving around a partially relaxed OH such as to cover the range between the optimum value at the saddle point and the one at the asymptote. Adapted with permission from Ref.[81] (Copyright 2013 American Institute of Physics).

were reported on both CHIPR and DMBE PESs using 3D time-dependent quantum wave-packet method [87]. As is visible from the reaction probabilities for $J=0$, the reactivity of $\text{OH}(v=0, J=0-5)+\text{O}$ reaction does not always increase with the rotational excitation of OH. As presented in FIG. 3, all theoretical rate constants have a negative temperature dependence over ~ 50 K and deviate substantially from the experiments of Carty *et al.* [45] at lower temperature. It may conclude that J -shifting method can only be utilized to determine thermal rate coefficients correctly. Full quantum mechanical calculations with larger J values are required for low temperatures. However, it is still difficult for the deep well reaction with large number of coupled states.

The first excited electronic state of $\text{HO}_2(\tilde{A}^2\text{A}')$ is degenerated with its ground state of $\tilde{X}^2\text{A}''$ at linear geometries and correlated to the same product of $\text{OH}+\text{O}$, which is associated with the reaction between the H atom and the singlet molecular oxygen molecule,



Thus, the reaction between $\text{H}+\text{O}_2(\tilde{X}^3\Sigma_{\text{g}}^-)$ and

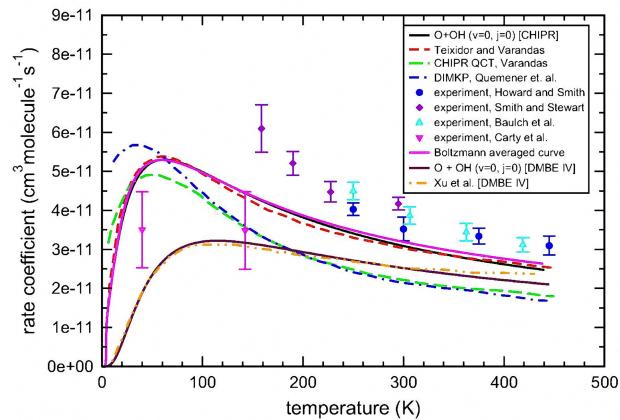


FIG. 3 Comparison of the theoretical rate coefficients for $\text{O}+\text{OH} \rightarrow \text{H}+\text{O}_2$ reaction. Adapted with permission from Ref.[87] (Copyright 2017 Elsevier B.V.).

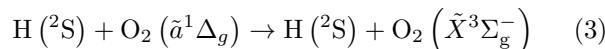
$\text{H}+\text{O}_2(\tilde{a}^1\Delta_{\text{g}})$ may compete via the so-called Renner-Teller effects in the collinear HO_2 complex, which is a non-Born-Oppenheimer effect for $J>0$, or the nonadiabatic coupling to the product asymptote of $\text{OH}+\text{O}$ as speculated in some theoretical [51, 63, 72, 75] and experimental [88, 89] studies in the former reaction. Unlike the $\text{H}+\text{O}_2(\tilde{X}^3\Sigma_{\text{g}}^-)$ reaction, the reaction path of the first excited electronic state is slightly exothermic with a significant barrier of 0.26 eV in the reactant valley, as shown in FIG. 1(a).

Earlier attempts of $\text{HO}_2(\tilde{A}^2\text{A}')$ PES either consisted of a small number of *ab initio* points [23] or did not cover the entire configuration space [28, 90, 91], which are unsuitable for dynamic studies. Recently, Li *et al.* [92] reported the first globally accurate PES of the first excited state ($\tilde{A}^2\text{A}'$) of HO_2 by spline-fitting 17000 *ab initio* points at the icMRCI level with the AVQZ basis set. The available experiment data, such as dissociation and vibrational energies, were accurately reproduced. With this PES, Ma *et al.* [93] calculated the basic dynamical properties of the reaction using exact quantum mechanical (EQM) method and statistical quantum mechanical (SQM) model. The forward-backward angular distributions of the OH product reveal that the reaction proceeds via a complex-forming mechanism, which is consistent with the formation of a long-lived HO_2 intermediate. However, the SQM calculations typically overestimate the total integral cross-section and underestimate the rotational excitation of the OH product, attributed to the dynamical bottlenecks. Subsequently, the detailed dynamical characteristics [94] including ICSs, differential cross-sections (DCSs), product state distributions, and thermal rate coefficients were carried out by QCT method on the same excited PES. Besides the aforementioned doublet state barrier, a quartet transition state (${}^4\text{A}''$) was also observed by Sharipov and Starik [95]. In this case, the interaction between H and ground state $\text{O}_2(\tilde{X}^3\Sigma_{\text{g}}^-)$ can

TABLE I Recommended rate constants for product channels of H+O₂($\tilde{a}^1\Delta_g$) reaction.

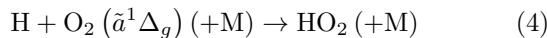
Reaction channels	Rate constants/(cm ³ /s)
All channels	$k_{\text{total}} = 3 \times 10^{-11} \cdot T^{0.17} \cdot \exp[-(2726 \pm 280)/T]$
OH($\tilde{X}^2\Pi$)+O(³ P)	$k_2 = 6.8 \times 10^{-16} \cdot T^{1.51} \cdot \exp[-(3040 \pm 200)/T]$
HO ₂ (+M)	$k_4 = k_{\text{total}} \cdot \frac{k_0 \cdot [M]}{k_{\text{total}} + k_0 \cdot [M]}$
H(² S)+O ₂ ($\tilde{X}^3\Sigma_g^-$)	$k_0 = 2.2 \times 10^{-37} \cdot T^{2.34} \cdot \exp(-1350/T), M = O_2$ $k_3 = k_{\text{total}} - k_2 - k_4$

occur via quartet PES and a collisional quenching channel of



also exists. The investigation of intersystem crossing between the second doublet PES and the lowest quartet PES is thus necessary, which should provide the possibility of considering the nonadiabatic transition between the H+O₂($\tilde{X}^3\Sigma_g^-$) and ($\tilde{a}^1\Delta_g$).

Furthermore, at high pressures, third-body collision is important in the following recombination reaction [96],



where M is a third molecule. This reaction can lead to the formation of the active complex HO₂* and stabilize it subsequently, making the reaction a chain-termination step. Indeed, HO₂* represents all the low energy resonances occurring in the scattering process of H+O₂(v_i, j_i) \rightarrow H+O₂(v_f, j_f).

Despite the long history of the research in the H+O₂($\tilde{a}^1\Delta_g$) reaction [46, 92, 94–101], the intrinsic mechanism of the reaction is still ambiguous. Recently, Chukalovsky *et al.* [102] carried out a comprehensive analysis of all available data evaluated from experiments, modeling, and theoretical estimations on the rate constants of possible channels. They argued that the non-adiabatic transition of the HO₂ complex from the first excited state (²A'') to the ground quartet state (⁴A'), assumed by Sharipov and Starik [95], was unable to interpret the discrepancy between experimental and theoretical rate constants of H+O₂($\tilde{a}^1\Delta_g$) and the high probability for reaction channel (3). It was known that the lowest doublet electronic states (²A'') and (²A') of HO₂ are degenerated in collinear geometries and rovibrationally coupling leads to Renner-Teller effect [15, 103]. The Renner-Teller coupling between ground state (²A'') and first excited state (²A') of HO₂ provides the probability of opening an additional dissociation channel of the excited HO₂ complex via atomic H and triplet molecular O₂($\tilde{X}^3\Sigma_g^-$) formation, which was suggested to account for the mechanism of the H+O₂($\tilde{a}^1\Delta_g$) reaction [102]. It revealed that the IVR process of excited HO₂(²A') is crucial in product channels. *Ab initio* calculations, taking into

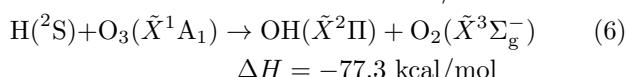
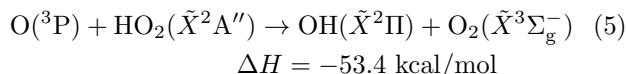
account both the lowest doublet states, may provide detailed information on both reaction and quenching channels. However, no such calculations have been performed yet. Thus, further extensive *ab initio* study is highly desirable. Based on those available data, the temperature dependence of H+O₂($\tilde{a}^1\Delta_g$) reaction rate constants was reproduced and the approximate Arrhenius expressions of the reactions were recommended (see Table I) [102]. The activation energy of the OH($\tilde{X}^2\Pi$)+O(³P) channel, 3040 K, was close to the entrance energy barrier, 3017 K (0.26 eV), of recent HO₂(²A') PES [92]. In addition, the pressure dependence of the H+O₂($\tilde{a}^1\Delta_g$)(+M) \rightarrow HO₂(+M) reaction was investigated by shock tube experiments [102], and the recommended expression is also shown in Table I.

Besides, three conical intersections exist between the ground state ($\tilde{X}A''$) and the excited state (\tilde{A}^2A') PESs of HO₂, including one occurring at C_{2v} geometry (that is, O—H—O) and the other two occur at linear geometries (that is, H—O—O and O—O—H). And it was found that the HO₂ PES around C_{2v} conical intersection lies lower in energy and could be easily encircled by low energy trajectories. The geometric phase (GP) effect [104, 105], also known as Berry's phase [106], stemming from the sign change of the Born-Oppenheimer adiabatic electronic wave function when the nuclei encircle a close path around a conical intersection, was shown to control the outcome of an ultracold (<1 mK) chemical reaction in the HO₂ system. Kendrick *et al.* [107–112] have performed numerous theoretical studies on GP effect by taking H+O₂ reaction as a prototype. In order to include GP effect in three-dimension quantum scattering calculations, Kendrick and Pack [107] have presented a general vector potential approach in hyper-spherical coordinates and a hybrid discrete variable representation and finite basis representation (DVR/FBR) numerical technique for C_{2v} conical intersection in HO₂. Subsequently, these methods were applied to include GP effect in H+O₂ scattering calculations for zero total angular momentum [108]. The results of significant shift in the resonance spectrum and significant changes in state-to-state transition probabilities manifest explicitly the key role of GP effect. These differences clearly demonstrated that GP effect should be crucial for H+O₂ scattering calculations and cannot be ignored even at low collision energy. Bound state

spectrum of HO₂ was also calculated with and without GP effect [109]. However, GP effect makes no difference in the vibrational energies even for extremely highlying states near dissociation. To further understand the mechanism and the rotationally and vibrationally resolved reaction rates in ultracold chemistry due to GP effect, scattering calculations of the O+OH(*v*=0, *j*=0)→H+O₂(*v'*, *j'*) reaction for *J*=0–5 have been carried out very recently [111, 112]. They draw an interference mechanism that the GP effect arises from the interference of the two scattering amplitudes between the direct and looping pathways. Both rotationally resolved reaction rates and vibrationally ones can be enhanced or suppressed nearly two orders of magnitude when the GP effect is included in calculations, as shown in Table II. For instance, reaction rate of 2.1×10^{-14} cm³/s for *j'*=3 at 1 μK with GP is about sixty times smaller than the corresponding one without GP (1.2×10^{-12} cm³/s), while the GP result (8.4×10^{-13} cm³/s) is over forty times larger than that without the GP (2.0×10^{-14} cm³/s) for *j'*=1. The external electric field was demonstrated to significantly modulate the GP effect, and it offers a probability that the GP effect can switch on or off the reactivity and play a role of “quantum switch” owing to the changed sign of the interference term [111]. Confusingly, the number of bound state structure in electric field does not switch between extreme values, +1 and -1, as expected. The real mechanism for Stark effect on GP effects still remains elusive. A more detailed investigation on GP effect with external electric field is highly demanded.

III. THE HO₃ SYSTEM

The hydrogen trioxy radical (HO₃) has been known as an important participant in the combustion [113–117], atmosphere chemistry [118–125], and biological processes [126–131]. It is also a very important open shell species in the atmosphere, formed by adduct of OH and O₂. In organic chemistry, HO₃ has been implicated as an intermediate in ozonation reactions [116, 132]. Two exothermic reactions



are proceeded on the HO₃(*X*²A'') ground state PES, which govern the HO_x radical concentration in the upper stratosphere [16] and mesosphere [17, 18] and play a significant role in the cycle for ozone depletion. The reaction pathways are shown in FIG. 1(b). In light of this importance, there have been many theoretical studies and experimental investigations on HO₃ system, as well as many kinetic studies for above reactions.

TABLE II Ultracold (1 μK) rates for O+OH(*v*=0, *j*=0)→H+O₂(*v'*, *j'*) reaction with (GP) and without (NGP) geometric phase effect. Data are extracted from Ref.[112].

<i>v'</i> , <i>j'</i>	Rates/(cm ³ /s)		<i>k</i> _{GP} / <i>k</i> _{NGP}
	<i>k</i> _{GP}	<i>k</i> _{NGP}	
<i>v'</i> =2, <i>j'</i> =1	8.4×10^{-13}	2.0×10^{-14}	42.00
<i>v'</i> =2, <i>j'</i> =3	2.1×10^{-14}	1.2×10^{-12}	0.02
<i>v'</i> =2, <i>j'</i> =5	4.7×10^{-12}	5.2×10^{-13}	9.04
<i>v'</i> =1 ^a	4.4×10^{-12}	8.3×10^{-12}	0.53
<i>v'</i> =2 ^a	4.7×10^{-12}	7.4×10^{-12}	0.64
Total ^b	2.0×10^{-11}	2.8×10^{-11}	0.71

^a Vibrationally resolved reaction rates summed over all open product vibrational level *j'*.

^b Total reaction rate summed over all open product vibrational and rotational state of O₂(*v'*, *j'*).

The HO₃ radical was first detected by Cacace *et al.* using neutralization-reionization mass spectrometry [133]. Its IR spectra have been reported in argon matrices [134] and in irradiated H₂O/O₂ ice mixtures [120, 135]. Rotational transitions for *trans*-HO₃ and *trans*-DO₃ in the gas phase were observed by Suma *et al.* using Fourier-transform microwave spectroscopy, but the *cis* ones were not observed [136]. Based on the derived rotational constants and theoretical calculations of dipole moments, they concluded that the *trans* planar isomer is a weakly bound molecule with a fairly long central O–O bond. In 2008, Derro *et al.* [137] measured the fundamental frequencies for each vibrational mode of HO₃ and DO₃ in the gas phase using IR-UV double resonance technique. The observed frequencies are significantly different from previous experimental and theoretical results. Harmonic vibrational frequencies have been calculated by Zhou *et al.* [138] using the explicitly correlated RCCSD(T)-F12, RS2(LS/IPEA), MRCI+Q, and MR-AQCC methods. However, the anharmonic effect is hard to be conclusive due to highly demanding in *ab initio* calculations. Braams and Yu [139] have done rigorous ro-vibrational calculations, based on a local PES calculated at HCTH/aug-cc-pVTZ level. Unfortunately, the vibrational energy levels show large discrepancies with experimental values [119, 137], due to the inaccuracy of the PES. To do the force field calculations, hundreds of points at the vicinity of the *trans*- and *cis*-HO₃ minima were calculated at MRCI+Q/AVQZ level by Suma *et al.* [140]. The calculated vibrational frequencies well reproduce the available experimental values, as shown in Table III. The elusive HO₃ radical, which is a very difficult system for *ab initio* characterization, has been characterized systematically using various benchmark *ab initio* methods, as reviewed in Ref.[141, 142]. However, there remain significant discrepancies between experiment and theory with respect

TABLE III Fundamental frequencies of HO₃ obtained from several experimental and theoretical studies.

	<i>v</i> ₆	<i>trans</i> -HO ₃				<i>cis</i> -HO ₃		
		Expt. [137]	UB3LYP/ VTZ [122]	HCTC/ AVTZ [139]	MRCI+Q/ AVQZ [140]	Expt. [137]	HCTC/ AVTZ [139]	MRCI+Q/ AVQZ [140]
Torsion	<i>v</i> ₆	128.7	282	176.80	124.7	149.1	198.73	160.7
Middle O–O stretching	<i>v</i> ₅	243.7	453	354.30	251.5	243.6	323.26	218.6
O–O–O bending	<i>v</i> ₄	481.9	652	649.99	485.7	486.5	663.81	648.5
H–O–O bending	<i>v</i> ₃	997.9	1199	1136.34	1015.2	1008.6		1160.4
End O–O stretching	<i>v</i> ₂		1341	1351.52				
O–H stretching	<i>v</i> ₁	3569.30	3548		3570.6	3565		3538.1

to its structural properties and stability, as summarized in Table IV. For example, the bond length of the central O–O bond ranges from 1.4 Å to 1.7 Å by different *ab initio* methods [117, 122, 136, 139, 143–151], while the experimental value is 1.688 Å [136] or 1.684 Å [152]. Numerous high-level *ab initio* results suggested that multi-reference methods predicted longer central O–O bond length. Besides, the relative stability between *trans*- and *cis*-HO₃ is different with different theoretical method. Some early *ab initio* theoretical work and DFT studies predicted a non-planar structure, while recent calculations reached consensus that HO₃ intermediate is planar with both *trans* and *cis* geometries. In 2011, Varandas [147] explored the MEP for isomerization of HO₃ using high-level *ab initio* methods with extrapolation to the complete basis set limit, as shown in FIG. 4. The results showed that, for single reference methods, the *cis*-HO₃ is slightly more stable than the *trans*-HO₃. In turn, the multi-reference calculations predicted that the *trans*-HO₃ is more stable, which is in agreement with the available experimental evidence.

In addition, there has been much debate on the binding energy of HO₃, as shown in Table IV. An upper limit of the dissociation energy was estimated to be 5.31 or 6.12 kcal/mol from experiments using infrared action spectroscopy [118, 119, 137, 153]. In 2010, Le Picard *et al.* [154] derived a value of (2.9±0.07) kcal/mol on the basis of experimental kinetic studies, in which the OH concentration was measured in the presence of excess O₂ using laser-induced fluorescence. A number of theoretical investigations at different levels of theory and basis set predicted 4–10 kcal/mol for the binding energy of HO₃ [139, 148, 150, 155, 156]. Most recently, Varandas [151] calculated the dissociation energies *D*_e, which are 4.5 and 4.7 kcal/mol for the *cis* and *trans* isomers, respectively. The *D*₀ value for *trans*-HO₃ is in good agreement with the commonly accepted value (2.9±0.07) kcal/mol from the low-temperature CRESU experiment. FIG. 5 shows the dissociation curves for the reaction HO₃→HO+O₂ at different levels of theory. The EOMIP-CCSD curve [148] predicted a significant barrier which is about 5 kcal/mol above the *trans* minimum and then drops steeply to reach the asymptote at 2.5 kcal/mol. The existence of such a barrier

TABLE IV A comparison of classical dissociation energies (*D*_e in kcal/mol) for HO₃→OH+O₂, dissociation energies at 0 K (*D*₀ in kcal/mol) and central O–O bond lengths (*r*_{O–O} in Å) for *trans*-HO₃ from different theoretical and experimental studies.

Method	<i>D</i> _e	<i>D</i> ₀	<i>r</i> _{O–O}
MCHF [143]	13.8		1.472
G2M2(RCC) [144]		1.3	1.543
MRMP2//CASSCF [117]	6.0	2.8	1.750
QCISD(T)-CBS [145]	5.3		1.495
CCSD(T)-CBS(W1U) [122]	3.4	0.1	1.544
MRCIQ+Q [136]	3.9		1.677
CCSD(T)//QCISD [146]	0.1	-3.9	1.522
MRCI+Q [146]	5.4	1.4	1.647
MRCI+Q//CASSCF [139]	3.5		1.544
MRCI+Q/VTZ [147]			1.695
HCTH [139]	9.9	6.2	1.610
CCSD(T) [148]	5.2	2.5	1.589
CCSD(T)-CBS [149]			1.582
CASPT2(13,11) [150]	5.4	2.6	1.734
CASPT2(19,15) [150]	5.8	3.0	1.682
MRCI+Q/VQZ [151]	4.7±0.1	2.7±0.2	1.691
Expt. [154]		2.9±0.07	
Expt. [136]			1.688
Expt. [152]			1.684

conflicts with the experimental evidence, in which a strong negative temperature dependence [154] for the reversed association reaction suggests a barrier-free reaction. This observation suggests that the commonly used single-reference CCSD approach might not be able to provide an accurate global PES, due apparently to the multi-reference characters of the system.

The first global PES for the ground state HO₃ (DMBE I) was constructed by Varandas and Yu [157] using UCISD method. The PES predicts a metastable HO₃ structure, which conflicts with the experimental evidence and high-level *ab initio* calculations. In 2001, Varandas *et al.* [145] obtained a new PES for this system using the QCISD(T)/CBS method, named

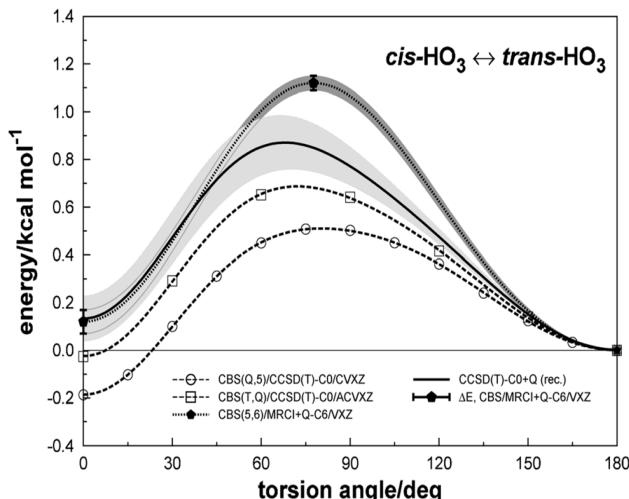


FIG. 4 The isomerization path of $\text{trans-HO}_3 \leftrightarrow \text{cis-HO}_3$. Adapted with permission from Ref.[147] (Copyright 2011 Royal Society of Chemistry).

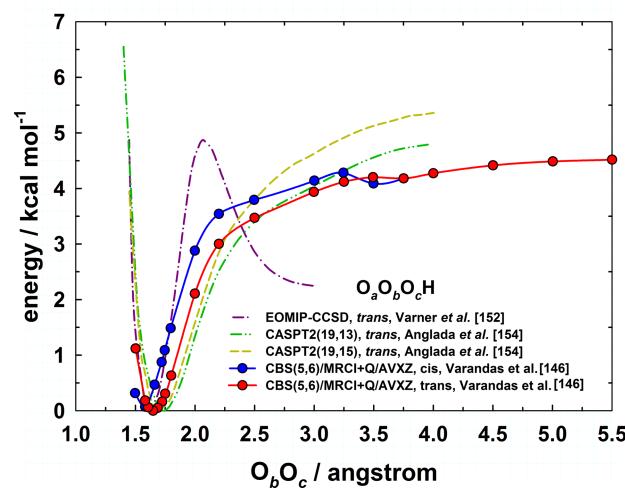


FIG. 5 Dissociation curves for the reaction $\text{HO}_3 \rightarrow \text{O}_2 + \text{OH}$ as it progresses from the *trans*- and *cis*- HO_3 geometries (energies taken relative to the *trans-HO*₃ minimum).

DMBE II. This PES has a dissociation barrier, which is inconsistent with the available experimental evidence, and two stable planar HO_3 isomers, in which the *cis*- HO_3 is more stable than the *trans* one. These PESs are not sufficiently accurate due to the low level of *ab initio* theory and to the relatively small number of *ab initio* points. Another analytical PES in the many body expansion form was obtained by fitting to about 28000 HCTH/aug-cc-pVTZ points [139]. The PES predicts a D_0 of 6.15 kcal/mol, and implies a central O–O bond length of 1.610 Å for *trans-HO*₃, which is shorter than the commonly accepted value of 1.688 Å. And the vibrational frequencies carried out on this PES have large discrepancies with the experimental results [119, 137].

Several kinetic measurements have been conducted to determine the rate constants for the $\text{O}+\text{HO}_2$

reaction [158–162], which can be used to simulate the concentrations of OH, HO_2 , and O_3 in the upper stratosphere and lower mesosphere. The reported rate coefficients of this exothermic reaction have a negative temperature dependence at low temperatures. The measured rate constant for the reaction $\text{O}+\text{HO}_2 \rightarrow \text{HO}+\text{O}_2$ was found to be independent with N_2 pressure from 10 torr to 500 torr with a mean value of $(6.2 \pm 1.1) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ at 298 K by Ravishankara *et al.* [162], which is in good agreement with the value of $(6.1 \pm 0.4) \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ reported by Keyser [158]. Brune *et al.* [160] and Sridharan *et al.* [163] reported that the rate constants for this reaction at 300 K are $(5.2 \pm 0.8) \times 10^{-11}$ and $\sim 5.7 \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$, respectively. In 1987, Nicovich *et al.* [161] employed a pulsed laser photolysis technique to investigate the kinetic of this reaction over the range of 266–391 K at 80 torr of N_2 . Their results followed the Arrhenius expression: $k(T) = (2.91 \pm 0.7) \times 10^{-11} \exp[(228 \pm 75)/T] \text{ cm}^3/(\text{molecule}\cdot\text{s})$. The rate constant recommended by the NASA kinetic data evaluation panel is an average of these five studies. However, the atmosphere chemistry reaction model using the recommended value for this reaction underestimated the ozone concentration in the mesosphere [17, 18]. Based on the DMBE I PES, the rate constant, product distributions, and differential cross sections for the reaction $\text{O}+\text{HO}_2 \rightarrow \text{HO}+\text{O}_2$ by employing the QCT method [164] and a reduced three-dimensional quantum dynamic method [165] showed large differences between themselves and the available experimental data. In the reduced-dimensional quantum mechanical study, the reaction was treated as coplanar and the infinite-order sudden approximation was applied, which gave too low values of rate constants and cross sections. In 2004, Silveira *et al.* [166] found that the vibrational excitation has minor effect on the dynamics based on the QCT calculations on the DMBE I and DMBE II PESs, respectively. In addition to the complex-forming pathway, this reaction can also proceed via a direct hydrogen abstraction pathway on two doublet (${}^2\text{A}''$ and ${}^2\text{A}'$) and two quadruplet (${}^4\text{A}''$ and ${}^4\text{A}'$) states. The abstraction barriers are approximately 2–4 kcal/mol based on *ab initio* calculations [117, 143]. As a result, this pathway will become viable at high temperatures and contribute to the rate constant.

Neither the complex-forming nor abstraction pathway was accurately described by the existing HO_3 PESs. To better understand the kinetics and dynamics of the relevant reactions, we suggested to map out new accurate global PESs of the ground and excited electronic states for this system using the MRCI-F12 approach and the permutation invariant polynomial neural network (PIP-NN) fitting approach [167]. The spin orbital couplings should also be included. The PESs will include the $\text{OH}+\text{O}_2$, $\text{O}+\text{HO}_2$, and $\text{H}+\text{O}_3$ channels, as well as the complex-forming and direct abstraction pathways. The PESs will greatly advance our under-

standing of the HO₃ system and associated reactions. We are particularly keen on obtaining accurate theoretical rate constants for the related reactions, which can be used to reduce uncertainties in combustion and atmosphere kinetic models. In addition, a full-dimensional quantum mechanical characterization for this system has not been accomplished due to the involvement of three heavy atoms and the deep potential wells. Further theoretical improvements on decreasing the number of basis and improving computational efficiency in quantum dynamic method are very desirable.

IV. SUMMARY

In this review, we have presented an overview of the recent progresses in two prototypical oxyhydrogen complex-forming reactions of the HO₂ and HO₃ systems. A number of achievements have been obtained from the unremitting efforts of numerous researchers, whereas there are still many questions to be illuminated. For HO₂, several global PESs for the ground electronic state have been constructed, and the predicted rate constants are in reasonable agreement with the available observed values, while some major discrepancies still exist. The nonadiabatic effect has been found to be crucial in the HO₂ system and nonadiabatic quantum dynamical calculations with excited PESs, including electronic states of 1²A'', 1²A', 2²A'' and 4²A'', are necessary. In particular, the influence of the GP effect on the reaction dynamics of O+OH($v=0, j=0$)→H+O₂(v', j') needs to be further addressed. Besides, different PESs predicted disparity state-to-state dynamics for the reaction of H+O₂, especially at higher collision energies, so that molecular beam experiment is very demanding to confirm the detailed reaction mechanism. For HO₃, only the minimum energy path on the ground electronic state has been widely investigated, but no reliable reaction dynamics for the related reactions are performed due to the absence of an accurate global PES and to the difficulty of carrying out quantum dynamics for such complex-forming reactions.

Thanks to the rapid development of the computing method and program of quantum chemistry, it is now feasible to perform high level *ab initio* calculation using MRCI-F12 for the electronic ground and excited states for the HO₂ and HO₃ systems. The artificial neural network (NN) method, which has been found to be the most efficient approach to fitting high dimensional PES [168], can be applied to generate the global PES for the ground and excited electronic states. Based on the accurate PESs, it is possible to perform the detailed quantum dynamics by employing the efficient wave packet propagation method. Although such dynamics calculations are still hard to implement for complex-forming reactions with a deep well, such as the reactions related to the HO₃ system, the computational efficiency could be remarkably improved by using the optimized coor-

dinates and suitable absorption in the boundary. With the close interplay between theory and experiment, it is anticipated that the detailed reaction dynamics for the reactions related to the HO₂ and HO₃ systems could be revealed in the near future.

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