

Mode Specificity in the  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  Reaction: Enhancement of Reactivity by Exciting a Spectator Mode

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**ABSTRACT:** A reaction typically involves a few active modes while the other modes are largely preserved throughout the reaction as spectators. Excitation of an active mode is expected to promote the reaction, but depositing energy in a spectator mode typically has no effect, because of the differing ability for energy flow to the reaction coordinate. In this work, we report a surprising case of mode specificity in a key radical–radical reaction  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ , where such canonical expectations fail to hold. Despite its spectator nature, the vibrational excitation of the OH reactant is shown at low collision energies to enhance the reactivity significantly. This unique effect can be attributed to the increased attraction with  $\text{HO}_2$  due to the larger dipole of the stretched OH. At low collision energies, the stronger attraction increases the chance of capturing the reactants to form a hydrogen-bonded complex, thus of passing through the submerged barrier. The novel mechanism differs from the conventional vibrational enhancement via coupling to the reaction coordinate at the transition state, enriching our understanding of mode specificity in chemistry.

Chemists have long recognized the differing capacity of chemical bonds in overcoming reaction barriers. Thanks to advances in laser techniques, it is now possible to prepare a single quantum state of a reactant and to measure the effect on reactivity. Indeed, ample evidence has been found that energies deposited in different reactant modes have disparate efficacies in promoting reactivity. Excitation of some reactant modes can significantly accelerate the reaction, while others are merely spectators that have little effect on reactivity. This so-called mode specificity and related bond selectivity have been extensively observed in both gaseous reactions<sup>1,2</sup> and reactions at gas–solid interfaces.<sup>3,4</sup>

Mode specificity has also been extensively investigated by theory, in which the reaction dynamics is simulated on multidimensional potential energy surfaces (PESs).<sup>5,6</sup> These dynamical calculations, whether quantum mechanical or quasi-classical, were made possible by our ever-improving capability in constructing accurate global reactive PESs from high-level *ab initio* data.<sup>7–11</sup> Such PESs are now sufficiently accurate to verify experimental observations and to predict dynamics, including mode specificity and bond selectivity in small reactive systems.<sup>5</sup>

To understand mode specificity, Polanyi proposed a set of rules for the  $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$  type reactions based on the location of the transition state (TS):<sup>12</sup> translational energy is more effective in overcoming an early barrier, while vibrational excitation has higher efficacy in surmounting a late barrier. These rules were extended to polyatomic systems with the Sudden Vector Projection (SVP) model,<sup>13,14</sup> which attributes the ability of a reactant mode in promoting a reaction to its projection onto the reaction coordinate at the TS. A large projection implies facile energy flow from the reactant mode to the reaction coordinate, thus promoting the reaction. For a spectator mode, the projection is, however, small or null, which inhibits energy flow into the reaction coordinate. The SVP

model has been applied to many reactive systems, and its validity is firmly established.<sup>15,16</sup> In several cases, the SVP model correctly predicted the mode specificity while Polanyi rules failed.<sup>17–19</sup>

Here, we report an extensive dynamical investigation of an important radical–radical reaction



in both atmospheric chemistry and combustion.<sup>20</sup> In the upper atmosphere, for example, R1 is a dominant pathway in removing OH and  $\text{HO}_2$ . These radicals are involved in several catalytic cycles involving other key atmospheric species, such as O,  $\text{O}_3$ ,  $\text{ClO}_x$ , and  $\text{NO}_x$ .<sup>21</sup> Under lean combustion conditions, R1 is a major consumption process of  $\text{HO}_2$  and responsible for the depletion of both radicals in burnt gases.<sup>22</sup> The rate coefficients of R1 ( $k_{\text{R1}}$ ) is difficult to measure because of its radical–radical nature and the accompanying side- and self-reactions.<sup>23</sup> The measured  $k_{\text{R1}}$  first decreases with temperature ( $T$ ) but increases with  $T$  as  $T$  increases.<sup>21,23–31</sup> This non-Arrhenius behavior signals a complicated mechanism for what Kaufman called a “Holy Grail” reaction.<sup>32</sup>

These experiments have stimulated many theoretical investigations of the reaction pathway and kinetics.<sup>29,30,32–39</sup> Very recently, a full-dimensional global PES for the ground triplet state of R1 was constructed from high-level *ab initio* data and the calculated  $k_{\text{R1}}$  was found to agree with experiment over a wide  $T$  range.<sup>40</sup> The availability of this PES allows a detailed study of the reaction dynamics, including mode specificity. In this Communication, we investigate the dynamics on the PES,

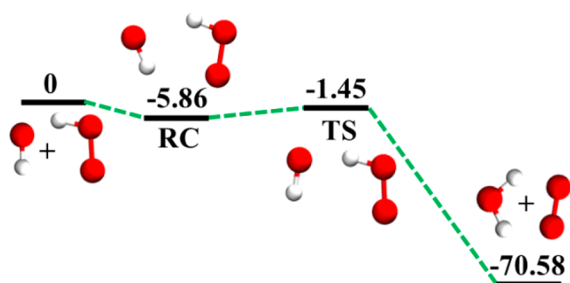
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using quasi-classical trajectory (QCT) and reduced-dimensional quantum dynamical (QD) approaches (details of calculations are given in the Supporting Information, SI). These studies reveal that the vibrational excitation of the OH reactant, which is considered a spectator mode, promotes the reaction significantly at low collision energies ( $E_c$ ). This unusual behavior is analyzed in detail, and the origin of the enhancement is identified.

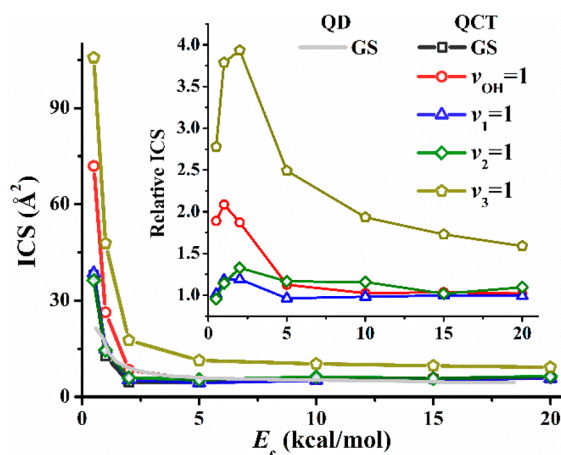
Figure 1 illustrates the reaction pathway, together with the geometries of the stationary points. The exoergic reaction is



**Figure 1.** Schematic energetics for R1 on the lowest triplet state PES. Energies are in kcal/mol and relative to the OH + HO<sub>2</sub> asymptote.

dominated by a hydrogen-bonded reactant complex (RC,  $-5.86$  kcal/mol), followed by a submerged barrier (TS,  $-1.45$  kcal/mol). As shown earlier,<sup>40</sup> the reaction mechanism is essentially direct and the submerged barrier leads to the negative  $T$ -dependence of the  $k_{R1}$  at low  $T$ .

Figure 2 presents the QCT excitation function, namely the integral cross section (ICS) as a function of  $E_c$  from the



**Figure 2.** QCT and QD excitation functions for OH( $\nu_{OH}$ ) + HO<sub>2</sub>( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ )  $\rightarrow$  H<sub>2</sub>O + O<sub>2</sub>, with relative ICSs (inset).

ground ro-vibrational states (GSs) of both reactants. The ICS drops drastically from  $E_c = 0.5$  to  $2.0$  kcal/mol and then rises slowly. The rapid decrease of ICS at low  $E_c$  stems apparently from a complex-forming mechanism.<sup>41</sup> Here, the complex is the hydrogen-bonded RC intermediate. At higher  $E_c$ , the reaction becomes activated due to the reaction bottleneck at TS.

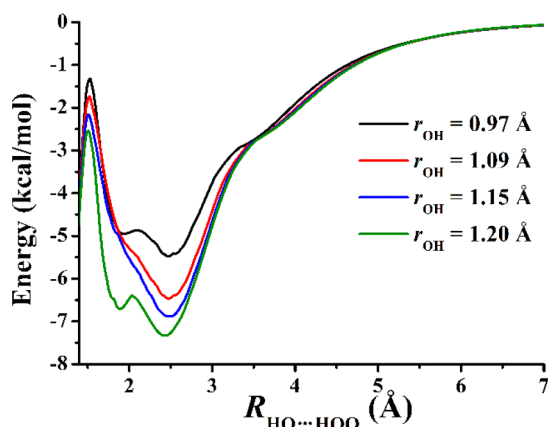
The QCT ICSs with fundamental excitations of  $\nu_{OH}$  of OH,  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  of HO<sub>2</sub> are shown in the same figure. Although all ICSs follow the same trend as the GS, they are significantly different, shown by the relative ICSs defined as  $ICS(\nu)/ICS(\nu = 0)$  in the inset of Figure 2. Indeed, the excitation in the H–

OO stretch ( $\nu_3$ ) shows a dramatic enhancement effect in the entire energy range, due apparently to the involvement of the transferring H. Excitations in the H–O–O bend ( $\nu_2$ ) and O–O ( $\nu_1$ ) stretch only have smaller enhancement effects on the reactivity at low  $E_c$ . However, OH vibrational excitation ( $\nu_{OH}$ ) shows a significant enhancement effect for  $E_c < 5.0$  kcal/mol, but no effect was found at higher energies. This enhancement is particularly surprising because this spectator mode is not involved in hydrogen abstraction. Indeed, the O–H distance of the OH moiety remains nearly constant along the minimum energy path of R1.<sup>40</sup>

Although the QCT method is efficient in studying polyatomic reactions, it does not describe quantum effects, such as tunneling, zero-point energy (ZPE), and resonances. To ascertain the validity of the QCT results, reduced-dimensional QD calculations from the reactant GSs were performed. As shown in Figure 2, the QD ICS agrees reasonably well with the QCT one: it first drops at low  $E_c$  and then becomes flat within 5–20 kcal/mol. The good agreement between QD and QCT results indicates that the quantum effects do not play a significant role in determining the trend of the reaction, confirming the reliability of the QCT results.<sup>42,43</sup> The QD ICSs with fundamental excitations in the reactants were not calculated due to excessively high computational costs.

To provide insight into the observed mode specificity, the SVP model is used. See SI for the illustration of the corresponding normal mode vectors. The calculated SVP values for the  $\nu_{OH}$ ,  $\nu_2$ ,  $\nu_1$ , and  $\nu_3$  modes are 0.020, 0.092, 0.329, and 0.508, respectively. These results suggest that the latter two modes of HO<sub>2</sub> are coupled with the reaction coordinate at the TS. The predictions are partially verified by the results in Figure 2. Not surprisingly, the H–OO stretching mode in the HO<sub>2</sub> reactant ( $\nu_3$ ) is strongly coupled with the reaction coordinate, as the hydrogen abstraction requires the motion of the transferring H atom. However, the  $\nu_{OH}$  mode has essentially no projection onto the reaction coordinate, and it can be considered as a spectator mode. The situation here is similar to the HF/HCl + OH  $\rightarrow$  F/Cl + H<sub>2</sub>O and H<sub>2</sub> + SH  $\rightarrow$  H + H<sub>2</sub>S reactions, where accurate QD calculations showed that the OH/SH vibration is indeed a spectator, consistent with their nearly zero SVP values.<sup>19,44,45</sup> However, this prediction is inconsistent with the QCT results for the title reaction.

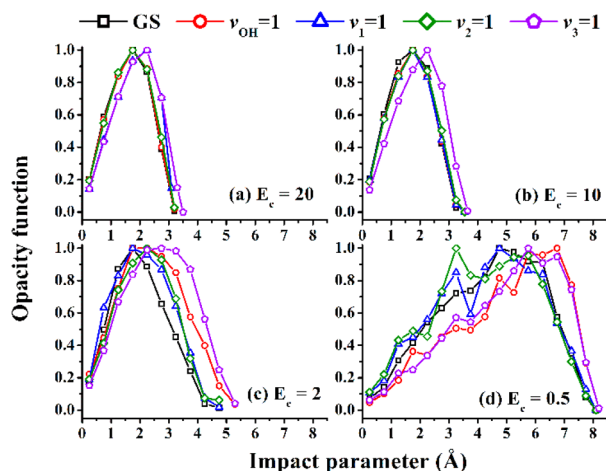
To identify the origin of the unexpected mode specificity concerning the stretching mode of the OH reactant, it is important to recognize the fact that the reaction barrier for R1 is below the reactant asymptote and there is a pre-TS well (RC), supported by a weak hydrogen bond between the two reactants. Consequently, the PES in the reactant asymptote is dominated by long-range forces, such as dipole–dipole interaction, between the two reactants.<sup>35</sup> As shown in the SI, the dipole of the OH species increases with the O–H bond distance within 0.6–1.2 Å. Therefore, we hypothesize that the excitation of the OH stretching mode increases its dipole and strengthens the hydrogen-bond interaction between the two reactants. To verify this, the interaction potential between the two reactants is plotted in Figure 3 for several O–H bond lengths. It is clear that the elongation of the OH bond leads to a deeper well for RC. At the outer turning point of OH( $\nu = 1$ ), namely  $R_{OH} = 1.20$  Å, the depth of the well is increased by about 1 kcal/mol, relative to the outer turning point of OH( $\nu =$



**Figure 3.** Interaction between OH and HO<sub>2</sub> (fixed at its equilibrium) along the  $R_{\text{OH}}$  distance at HO $\cdots$ HOO well.

0),  $R_{\text{OH}} = 1.09$  Å. In addition, the corresponding barrier is also lowered.

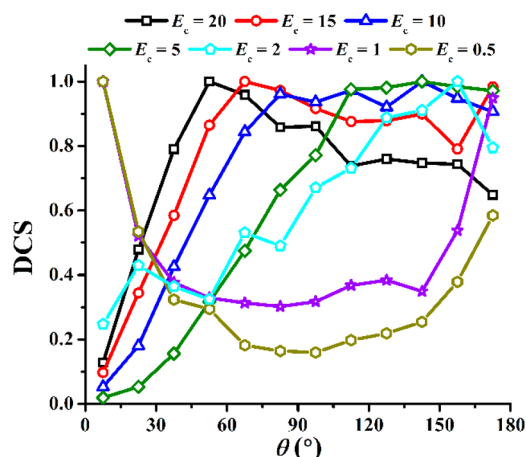
At low  $E_c$ , deepening the RC well enhances the capture of reactants, thus promoting the overcoming of the submerged reaction barrier, which is also lowered. This prediction is borne out in Figure 4, where QCT opacity functions are presented.



**Figure 4.** QCT opacity functions for several initial conditions at different  $E_c$  (in kcal/mol).

As  $E_c$  decreases, the accessible impact parameter increases significantly, indicating more effective capturing. Since RC has a very similar geometry to TS, the capture of reactants by the RC is expected to channel the flux to the TS, thus enhancing reactivity. This is further helped by the lowered barrier. Importantly, the reactivity enhancement by exciting the OH vibration in R1 is not due to the coupling with the reaction coordinate at the TS, thus not predicted by the SVP model. Rather, it has a different mechanism via the increased capture by the pre-TS well. This novel feature is possible as the unique reaction path consisting of a relatively deep RC well and a low and submerged reaction barrier. For the HF/HCl + OH  $\rightarrow$  F/Cl + H<sub>2</sub>O reactions, the former condition is satisfied, but the barriers are too high.

The formation of a long-lived RC complex also manifests in differential cross sections (DCSs), as shown in Figure 5 for GS. At low  $E_c$ , the DCS is largely forward–backward symmetric, suggesting a relatively long lifetime of the reaction complex.



**Figure 5.** QCT DCSs at different  $E_c$  (in kcal/mol) for GS reactants.

With  $E_c$  increases, DCSs become dominated by the backward and sideways scattering, suggesting direct rebound and/or stripping mechanisms. See SI for further discussions.

It is interesting to note that the switching of reaction mechanisms manifested in DCSs is intimately related to the non-Arrhenius kinetics of R1, both governed by the unique PES topography. At low  $T$ ,  $k_{\text{R1}}$  depends negatively on  $T$ , but it changes to a positive one at higher  $T$ .<sup>40</sup> This is because the reaction at low  $T$  is dominated by a complex-forming mechanism via capture by the RC well, characterized by a negative  $T$ -dependence. At higher  $T$ , the reaction becomes activated because of the bottleneck formed near the submerged barrier, resulting in Arrhenius behavior.

The type of reaction path found in the OH + HO<sub>2</sub> reaction is quite prevalent in reactions involving radical reactants, which are of great importance in combustion and atmospheric chemistry.<sup>46,47</sup> The barrier for such a reaction is typically low or submerged, and there is often a pre-TS well. Such a reaction path is known to lead to complicated and non-Arrhenius kinetics,<sup>47</sup> and the mode specificity discussed here is probably also quite common, particularly when OH is involved.

The QCT calculations also yield product state distributions. As discussed in the SI, the H<sub>2</sub>O and O<sub>2</sub> products are internally excited, as predicted by the SVP model.

To summarize, we report the first dynamical study of the OH + HO<sub>2</sub>  $\rightarrow$  H<sub>2</sub>O + O<sub>2</sub> reaction on a global full-dimensional PES using both QCT and reduced-dimensional QD approaches. This “Holy Grail” reaction has complicated kinetics due to its unique reaction path energetics, which also manifests in mode-specific dynamics. The key observation here is that vibrational excitation of the spectator O–H mode can significantly enhance the reactivity at  $E_c < 5$  kcal/mol. Unlike the conventional mode specificity, this surprising enhancement of reactivity is attributed to the increased dipole of the vibrationally excited OH, which strengthens the attraction between OH and HO<sub>2</sub>. The deepening of the pre-TS well facilitates the capture at low  $E_c$ , thus enhancing the reactivity. This work presents the first demonstration of vibrational control of chemical reactivity by exciting a spectator bond, enriching our understanding on mode-specific chemistry. Such a mechanism might be quite prevalent in reactions involving free radicals.



## ■ ASSOCIATED CONTENT

## ■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b12467>.

Details of theoretical methods and additional results (PDF)

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## Notes

The authors declare no competing financial interest.

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