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# Quantum Dynamics of the $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ Reaction on an Accurate ab Initio Potential Energy Surface

Shi Ying Lin and Hua Guo\*

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Pascal Honvault\*

Laboratoire de Physique Moléculaire, UMR CNRS 6624, Université de Franche-Comté, Campus de la Bouloie, UFR Sciences et Techniques 25030 Besançon cedex, France

Daigian Xie\*

Institute of Theoretical and Computational Chemistry, Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

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We report exact time-dependent and time-independent quantum mechanical studies of the title reaction on an accurate ab initio potential energy surface of Xu et al. (*J. Chem. Phys.* **2005**, 122, 24305). The  $J = 0$  reaction probabilities for several reactant states show sharp resonance structures superimposed on relatively low backgrounds, and they are remarkably different from existing quantum results on an earlier potential energy surface (DMBE-IV). The new findings reported here suggest that our current understanding of this important reaction might require significant revision.

## I. Introduction

Given its importance in combustion of hydrocarbons,<sup>1</sup> it is not surprising that the title reaction has attracted extensive experimental and theoretical interest. The relevant  $X^2A''$  ground electronic state potential is dominated by a  $\text{HO}_2$  well and a barrierless reaction path. Much effort has been devoted to the construction of a global potential energy surface (PES).<sup>2–5</sup> Among them, the DMBE-IV PES of Varandas and co-workers<sup>3</sup> has been widely used in dynamics studies of the title reaction.<sup>3,6–17</sup>

The DMBE-IV PES is more than 15 year old, and there have been several recent studies questioning its accuracy.<sup>18,19</sup> In an effort to improve our understanding of this important system, Xu, Xie, Zhang, Lin, and Guo (XXZLG) reported in 2005 a new global PES of  $\text{HO}_2(X^2A'')$  based on a spline fit of  $\sim 15\,000$  high quality ab initio points at the icMRCI+Q/aug-cc-pVQZ level of theory.<sup>20</sup> This PES provided a much improved agreement with experimental fundamental vibrational frequencies (errors  $< 10\text{ cm}^{-1}$  as opposed to  $\sim 100\text{ cm}^{-1}$  on the DMBE-IV PES).<sup>20</sup> Interestingly, the recently calculated vibrational spectrum of  $\text{HO}_2$  up to the dissociation limit indicated that the density of states on the DMBE-IV PES was substantially overestimated.<sup>21</sup> As a result, vibration of the highly excited  $\text{HO}_2$  radical and its unimolecular decay are not purely chaotic as suggested by early work on the DMBE-IV PES,<sup>22–24</sup> underscoring the inadequacy of this PES in describing the nuclear dynamics of this system.

These new findings strongly suggest that our current knowledge of the title reaction based on the DMBE-IV PES might also be in need of revision. In this letter, we report exact

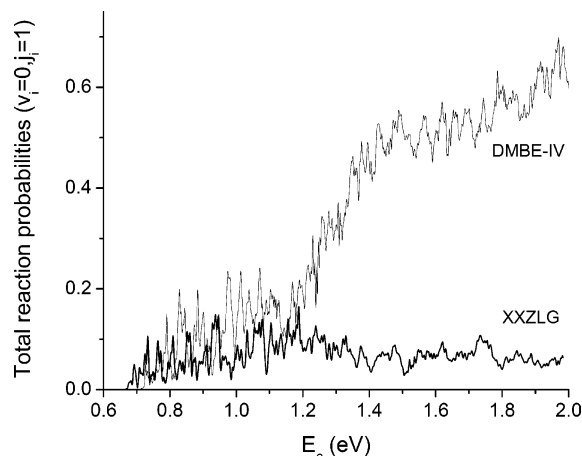
quantum mechanical calculations of the state-resolved reaction probabilities ( $J = 0$ ) on the new ab initio PES of Xu et al.<sup>20</sup> Both time-dependent and time-independent quantum mechanical (TDQM and TIQM) methods were used and the results on the two PESs are compared. The work reported in this letter represents our initial step toward the full elucidation of the reaction dynamics of this important combustion reaction.

## II. Methods

In the TDQM treatment, the wave packet was propagated in the Chebyshev order domain, which has been shown to be equivalent to time.<sup>25,26</sup> This numerically accurate and efficient propagation scheme has been applied in reaction dynamics,<sup>27,28</sup> where the outgoing boundary conditions for reactive scattering can be enforced using asymptotic damping terms.<sup>29</sup> The details of our method for calculating the S-matrix elements are given in a recent publication,<sup>30</sup> in which successful applications to the  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$  and  $\text{N}(^2\text{D}) + \text{H}_2 \rightarrow \text{NH} + \text{H}$  reactions were reported. Essentially, an internal state specified initial wave packet in the reactant channel was propagated in the product Jacobi coordinates and projected to the product internal states along the propagation as Chebyshev correlation functions. The S-matrix elements were then obtained by Fourier transform of these correlation functions. As an independent check, the total reaction probabilities were also obtained directly in the reactant Jacobi coordinates using a flux scheme<sup>31</sup> and found to be in excellent agreement with the sum of the state-resolved ones. Consequently, only the results of the state-to-state approach are reported here. The details of calculations, including discretization and convergence tests, will be reported in a future publication, along with the  $J > 0$  results.

We have also carried out TIQM scattering calculations using a method based on body-frame hyperspherical democratic

\* Corresponding authors. E-mail: hguo@unm.edu (H.G.); pascal.honvault@univ-fcomte.fr (P.H.); dqxie@mail.nju.edu.cn (D.X.).



**Figure 1.** Initial state ( $v_i = 0, j_i = 1$ ) specified total reaction probabilities ( $J = 0$ ) on the DMBE-IV (thin line) and XXZLG PESs (thick line) obtained from the TDQM method.

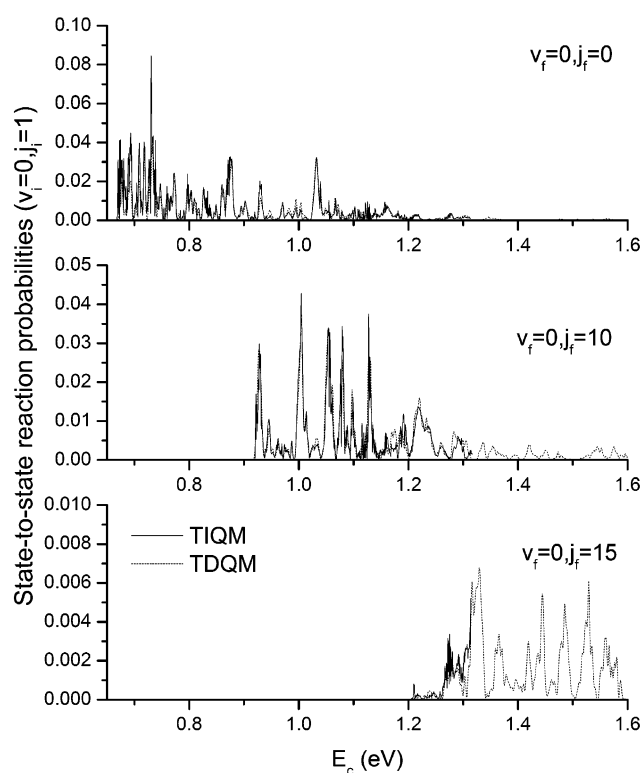
coordinates. This method was presented in detail in ref 32, and thus, a brief summary will suffice here. At each hyperradius  $\rho$ , the scattering wave function is expanded on a set of hyperspherical adiabatic states of a reference Hamiltonian  $H = T + V$  which incorporates the kinetic energy  $T$  arising from deformation at fixed hyperradius and the potential energy  $V$ . The expansion coefficients are the solution of a set of coupled second-order differential equations which are solved using the Johnson–Manolopoulos log-derivative propagator.<sup>33</sup> The adiabatic states are obtained by a variational expansion on a basis of hyperspherical harmonics. At small hyperradius, they span a large fraction of configuration space and allow for atom exchange. At large hyperradius, the adiabatic states concentrate into the arrangement valleys and describe  $O_2$  and  $OH$  molecules. This method has previously proved successful in describing the quantum dynamics of atom–diatom insertion reactions such as  $N(^2D) + H_2 \rightarrow NH + H$ ,<sup>34,35</sup>  $O(^1D) + H_2 \rightarrow OH + H$ ,<sup>36,37</sup>  $C(^1D) + H_2 \rightarrow CH + H$ ,<sup>38</sup>  $S(^1D) + H_2 \rightarrow SH + H$ ,<sup>39</sup> and also ultracold alkali–dialkali collisions.<sup>40,41</sup>

### III. Results and Discussion

In the TDQM calculations, 40 000 Chebyshev steps were used to propagate the wave packet initially placed in the reactant channel. The final state projection was performed at  $R_\infty = 12.0a_0$ . For the two radial coordinates, a  $449 \times 224$  direct product grid was used to cover the area defined by  $R \in (0.5, 18.0)a_0$  and  $r \in (0.5, 14.0)a_0$ . A large  $R$  grid is needed to accommodate the long-range potential in the exit channel. For the Jacobi angle, 100 DVR points were used which corresponds to  $j_{\max} = 99$ . This is a conservative grid size and no optimization was attempted. The grid for the direct calculation of the total reaction probability was significantly smaller because of symmetry adaptation in the reactant Jacobi coordinates and the smaller  $OH$ – $O$  distance where the projection is made. The corresponding propagation is also shorter ( $\sim 25$  000) because of the avoidance of final state projection.

In the TIQM calculations, we included 350 adiabatic states which correlate to rovibrational states of  $O_2$  with vibrational quantum numbers  $v = 0, 1, \dots, 8$  and odd rotational quantum numbers up to  $j_{\max} = 95, 89, 83, 77, 71, 63, 55, 43$ , and 31 and to rovibrational states of  $OH$  with vibrational quantum number  $v = 0, 1$ , and 2 and all rotational quantum numbers up to  $j_{\max} = 20, 14$ , and 5. This basis guarantees convergence below  $E_c = 1.3$  eV.

In Figure 1, initial state ( $v_i = 0, j_i = 1$ ) specified total reaction probabilities ( $J = 0$ ) for the DMBE-IV and XXZLG PESs are

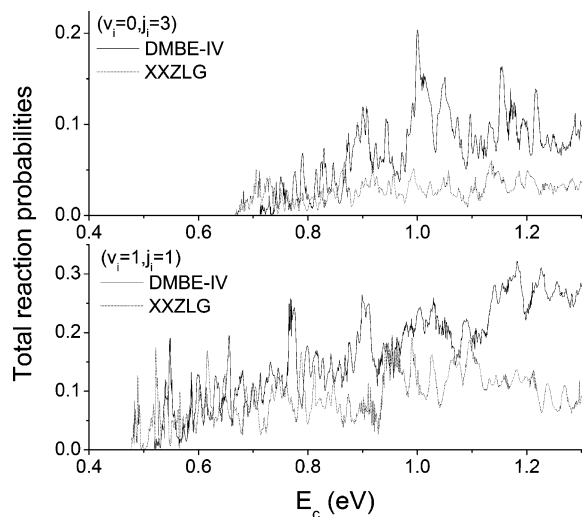


**Figure 2.** Product internal state resolved reaction probabilities ( $J = 0$ ) for the  $v_i = 0, j_i = 1$  reactant on the XXZLG PES. The TDQM and TIQM results are given in solid and dotted lines, respectively.

compared. The large differences of reactivity on the two PESs are striking. In particular, the reactivity on the DMBE-IV PES is larger than that on the XXZLG PES, especially for  $E_c > 1.2$  eV, and the former has a slightly higher reaction threshold. Meijer and Goldfield have attributed the sudden rise of the reaction probability near 1.2 eV to the onset of a direct reaction mechanism.<sup>14</sup> The sharp increase of reactivity on the DMBE-IV PES above 1.2 eV is absent on the new XXZLG PES, suggesting that the direct channel might be an artifact of the earlier PES. On the new PES, the reactivity actually decreases with collision energy, which is consistent with the kinematics; the light H at high speed is likely to be bounced back by the heavy  $O_2$  by the repulsive wall of the PES.

Similar to the DMBE-IV PES, the XXZLG PES gives rise to many narrow oscillatory features in the reaction probability, particularly at low energies. These features are apparently due to long-lived resonance states supported by the  $HO_2$  potential well. Such resonances could facilitate a statistical approximation of the reaction dynamics.<sup>21</sup> At high energies, the broader peaks presumably signify shorter lifetimes for the resonances.

In Figure 2, we displayed state-to-state reaction probabilities on the XXZLG PES with the  $v_i = 0, j_i = 1$  initial state, obtained from both the TDQM and TIQM methods. The agreement between the two numerically very different methods is quite satisfactory, as shown by the near perfect coincidences of the curves in Figure 2. The state-to-state reaction probabilities in Figure 2 appear to maximize near the corresponding thresholds and decrease with increasing energy. They are also dominated by long-lived resonances. In fact, the product ( $OH$ ) internal state distribution (not shown here) is highly sensitive to the dominating resonance(s) near the particular collision energy of interest. Overall, the internal degrees of freedom of  $OH$  are excited, indicative of the complex decaying dynamics of these resonances.



**Figure 3.** Total reaction probabilities ( $J = 0$ ) for rotationally or vibrationally excited reactants on the DMBE-IV (thin lines) and XXZLG PESs (thick lines) obtained from the TIQM method.

The total reaction probabilities with rotational and/or vibrational excited reactants are illustrated in Figure 3. Because of the good agreement between the two quantum mechanical methods, only results from the TIQM calculations are plotted. As in Figure 1, the reaction probabilities are dominated by long-lived resonances. It appears that the excitation of the internal state of the reactant  $O_2$  does not significantly enhance the reactivity. This is consistent with the notion that the title reaction proceeds largely via a complex-forming mechanism,<sup>42</sup> at least near the reaction threshold. Similar to the  $v_i = 0, j_i = 1$  case (Figure 1), it is also clear from the figure that the large differences between the two PESs persist and the reactivity on the XXZLG PES is generally smaller.

#### IV. Conclusion

In this letter, we report exact total and state-to-state quantum mechanical reaction probabilities of the  $H + O_2$  reaction ( $J = 0$ ) using the new XXZLG PES<sup>20</sup> which is based on spline fitting of 15 000 high level ab initio data and compare our results with those on the earlier DMBE-IV PES. Two different quantum methods were used, and the agreement was found to be excellent. The time-dependent approach generates a column of the S-matrix in the entire energy range from each propagation but scales more favorably with the dimensionality of the problem. On the other hand, the time-independent approach computes the entire S-matrix but has to repeat the calculation at many energies.

Although the reaction probabilities on both PESs are found to be highly oscillatory due apparently to long-lived resonances supported by the  $HO_2$  potential well, significant smaller reactivity was found on the XXZLG PES, particularly at high ( $E_c > 1.2$  eV) collision energies. The latter also has a lower reaction threshold. The initial rotational or vibrational excitation in the  $O_2$  reactant was found to have a minor effect on the reactivity.

Since the  $J = 0$  reaction probability has an insignificant contribution to the reaction cross section or rate constants at combustion temperatures, it is hard to say at this moment how large an impact the new ab initio PES would have on the reaction dynamics. To this end, we are performing both quasi-classical trajectory and exact quantum studies on the new PES. Our preliminary quantum results for  $J > 0$  indicate that significant discrepancy with the existing dynamic results on the DMBE-IV PES persists. Since the observed discrepancy is

obviously due to the differences in the PESs, one should be extremely cautious in interpreting the dynamics of this important combustion reaction using the earlier DMBE-IV PES.

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#### References and Notes

- (1) Miller, J. A.; Kee, R. J.; Westbrook, C. K. *Annu. Rev. Phys. Chem.* **1990**, *41*, 345.
- (2) Melius, C. F.; Blint, R. J. *Chem. Phys. Lett.* **1979**, *64*, 183.
- (3) Pastrana, M. R.; Quintales, L. A. M.; Brandao, J.; Varandas, A. J. C. *J. Phys. Chem.* **1990**, *94*, 8073.
- (4) Walch, S. P.; Duchovic, R. J. *J. Chem. Phys.* **1991**, *94*, 7068.
- (5) Kendrick, B.; Pack, R. T. *J. Chem. Phys.* **1995**, *102*, 1994.
- (6) Varandas, A. J. C. *J. Chem. Phys.* **1993**, *99*, 1076.
- (7) Zhang, D. H.; Zhang, J. Z. H. *J. Chem. Phys.* **1994**, *101*, 3671.
- (8) Pack, R. T.; Butcher, E. A.; Parker, G. A. *J. Chem. Phys.* **1995**, *102*, 5998.
- (9) Kendrick, B.; Pack, R. T. *J. Chem. Phys.* **1997**, *106*, 3519.
- (10) Miller, J. A.; Garrett, B. C. *Int. J. Chem. Kinet.* **1997**, *29*, 275.
- (11) Germann, T. C.; Miller, W. H. *J. Phys. Chem. A* **1997**, *101*, 6358.
- (12) Viel, A.; Leforestier, C.; Miller, W. H. *J. Chem. Phys.* **1998**, *108*, 3489.
- (13) Dai, J.; Zhang, J. Z. H. *J. Phys. Chem.* **1996**, *100*, 6898.
- (14) Meijer, A. J. H. M.; Goldfield, E. M. *J. Chem. Phys.* **1998**, *108*, 5404.
- (15) Meijer, A. J. H. M.; Goldfield, E. M. *J. Chem. Phys.* **1999**, *110*, 870.
- (16) Goldfield, E. M.; Meijer, A. J. H. M. *J. Chem. Phys.* **2000**, *113*, 11055.
- (17) Sultanov, R. A.; Balakrishnan, N. *J. Phys. Chem. A* **2004**, *108*, 8759.
- (18) Yang, C.-Y.; Klippenstein, S. J. *J. Chem. Phys.* **1995**, *103*, 7287.
- (19) Harding, L. B.; Maergoiz, A. I.; Troe, J.; Ushakov, V. G. *J. Chem. Phys.* **2000**, *113*, 11019.
- (20) Xu, C.; Xie, D.; Zhang, D. H.; Lin, S. Y.; Guo, H. *J. Chem. Phys.* **2005**, *122*, 244305.
- (21) Lin, S. Y.; Xie, D.; Guo, H. *J. Chem. Phys.* **2006**, *125*, 091103.
- (22) Mandelshtam, V. A.; Grodzanov, T. P.; Taylor, H. S. *J. Chem. Phys.* **1995**, *103*, 10074.
- (23) Dobbyn, A.; Stumpf, M.; Keller, H.-M.; Schinke, R. *J. Chem. Phys.* **1995**, *103*, 9947.
- (24) Dobbyn, A.; Stumpf, M.; Keller, H.-M.; Schinke, R. *J. Chem. Phys.* **1996**, *104*, 8357.
- (25) Chen, R.; Guo, H. *J. Chem. Phys.* **1996**, *105*, 3569.
- (26) Gray, S. K.; Balint-Kurti, G. G. *J. Chem. Phys.* **1998**, *108*, 950.
- (27) Althorpe, S. C.; Clary, D. C. *Annu. Rev. Phys. Chem.* **2003**, *54*, 493.
- (28) Guo, H. In *Theory of Chemical Reaction Dynamics*; Lagana, A., Lendvay, G., Eds.; Kluwer: Dordrecht, The Netherlands, 2004; p 217.
- (29) Mandelshtam, V. A.; Taylor, H. S. *J. Chem. Phys.* **1995**, *103*, 2903.
- (30) Lin, S. Y.; Guo, H. *Phys. Rev. A* **2006**, *74*, 022703.
- (31) Lin, S. Y.; Guo, H. *J. Chem. Phys.* **2003**, *119*, 11602.
- (32) Honvault, P.; Launay, J.-M. In *Theory of Chemical Reaction Dynamics*; Lagana, A., Lendvay, G., Eds.; Kluwer: Dordrecht, The Netherlands, 2004.
- (33) Manolopoulos, D. E. *J. Chem. Phys.* **1986**, *85*, 6425.
- (34) Honvault, P.; Launay, J.-M. *J. Chem. Phys.* **1999**, *111*, 6665.
- (35) Balucani, N.; Cartechini, L.; Capozza, G.; Segoloni, E.; Casavecchia, P.; Volpi, G. G.; Aoiz, F. J.; Banares, L.; Honvault, P.; Launay, J.-M. *Phys. Rev. Lett.* **2002**, *89*, 013201.
- (36) Honvault, P.; Launay, J.-M. *J. Chem. Phys.* **2001**, *114*, 1057.
- (37) Aoiz, F. J.; Banares, L.; Castillo, J. F.; Brouard, M.; Denzer, W.; Vallance, C.; Honvault, P.; Launay, J.-M.; Dobbyn, A. J.; Knowles, P. J. *Phys. Rev. Lett.* **2001**, *86*, 1729.
- (38) Banares, L.; Aoiz, F. J.; Honvault, P.; Bussery-Honvault, B.; Launay, J.-M. *J. Chem. Phys.* **2003**, *118*, 565.
- (39) Banares, L.; Castillo, J. F.; Honvault, P.; Launay, J.-M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 627.
- (40) Soldan, P.; Cvitas, M. T.; Hutson, J. M.; Honvault, P.; Launay, J.-M. *Phys. Rev. Lett.* **2002**, *89*, 153201.
- (41) Cvitas, M. T.; Soldan, P.; Hutson, J. M.; Honvault, P.; Launay, J.-M. *Phys. Rev. Lett.* **2005**, *94*, 033201.
- (42) Lin, S. Y.; Rackham, E. J.; Guo, H. *J. Phys. Chem.* **2006**, *110*, 1534.