Formation of molecular oxygen in ultracold O+OH collisions

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We discuss the formation of molecular oxygen in ultracold collisions between hydroxyl radicals and atomic oxygen. A time-independent quantum formalism based on hyperspherical coordinates is employed for the calculations. Elastic, inelastic, and reactive cross sections as well as the vibrational and rotational populations of the product O₂ molecules are reported. A *J*-shifting approximation is used to compute the rate coefficients. At temperatures T=10-100 mK for which the OH molecules have been cooled and trapped experimentally, the elastic and reactive rate coefficients are of comparable magnitude, while at colder temperatures, T < 1 mK, the formation of molecular oxygen becomes the dominant pathway. The validity of a classical capture model to describe cold collisions of OH and O is also discussed. While very good agreement is found between classical and quantum results at T=0.3 K, at higher temperatures, the quantum calculations predict a larger rate coefficient than the classical model, in agreement with experimental data for the O+OH reaction. The zero-temperature limiting value of the rate coefficient is predicted to be about 6×10^{-12} cm³ molecule⁻¹ s⁻¹, a value comparable to that of barrierless alkali-metal atom-dimer systems and about a factor of five larger than that of the tunneling dominated F+H₂ reaction.

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I. INTRODUCTION

Important experimental progress is being made in creating ultracold molecules in tightly bound vibrational levels [1]. Very recently, formation of ground state molecules in the vibrational level v=0 has been reported by different groups for homonuclear molecules such as Cs_2 [2,3] and Rb_2 [4], as well as for heteronuclear polar molecules such as RbCs [5], KRb [6], and LiCs [7]. There has also been much progress in the measurement of rate coefficients of barrierless reactions involving alkali-metal atoms at cold and ultracold temperatures. This includes atom-molecule collisions such as Rb +Rb₂ [8,9], Cs+Cs₂ [10,11], Na+Na₂ [12], Rb or Cs +RbCs [13], and molecule-molecule collisions such as Cs₂ $+Cs_{2}$ [10,14], Na₂+Na₂ [12], and Rb₂+Rb₂ [9]. The typical rate coefficients of these reactions are on the order of $10^{-11}-10^{-10}$ cm³ molecule⁻¹ s⁻¹ depending on the collisional system, the temperature, and the vibrational levels probed. All these experimental studies indicate that inelastic and reactive processes occur at significant rates at ultracold temperatures, in accordance with theoretical predictions on barrier reactions [15-20] as well as a number of alkali-metal atom-dimer systems [21-30] such as Li+Li₂, Na+Na₂, and $K+K_2$ which proceed without an energy barrier in the entrance channel. The alkali-metal systems are characterized by triatomic complexes with deep potential wells which make them challenging systems for accurate quantum calculations. For these heavy systems, the density of triatomic states is large and it leads to strong couplings between them, enhancing inelastic quenching or reactive scattering [31]. However, explicit quantum calculations of molecule-molecule systems involving alkali-metal atoms are computationally intractable. In a recent theoretical study of vibrational relaxation in collisions between H_2 molecules, Quéméner *et al.* [32] showed that the relaxation rate coefficients at ultralow temperature can attain large values for some near-resonant processes which involve simultaneous conservation of internal energy and total internal rotational angular momentum of the colliding molecules.

While there have been a number of theoretical studies of ultracold reactive collisions of tunneling-dominated reactions with chemically distinct reactants and products [15-20], there have been no such studies involving barrierless chemical reactions at ultracold temperatures. Here we investigate the exothermic reaction

$$O(^{3}P) + OH(^{2}\Pi) \rightarrow H(^{2}S) + O_{2}(^{3}\Sigma_{g})$$
(1)

at cold and ultracold temperatures as an example of a barrierless chemical reaction involving non-alkali-metal atoms. The reaction is of key interest in oxygen chemistry in the interstellar medium, OH chemistry in the upper stratosphere and mesosphere, and combustion chemistry (see Ref. [33] and references therein). The OH radical has also been cooled and trapped using the buffer gas and Stark decelerator techniques [34–37]. High-precision measurements of its radiative lifetime [38] and its hyperfine constant [39,40] have recently been reported. An experimental study of scattering between cold OH molecules and He atoms and D₂ molecules has recently been reported [41]. The cooling and trapping studies have stimulated a number of theoretical investigations involving the OH molecule in the last few years. González-Sánchez et al. [42] reported rotational relaxation and spin flipping of OH in He collisions at ultralow energies. They found that rotational relaxation occurs more efficiently than elastic collisions at vanishing collision energies. By carrying out quantum calculations of Rb+OH collisions at ultracold temperatures Lara et al. [43,44] explored the possibility of sympathetic cooling of OH molecules by collisions with Rb atoms. They argued that efficient sympathetic cooling of OH molecules in the ground vibrational state by collisions with Rb atoms is unlikely to occur due to the large inelastic rate coefficient. External fields can also have important effects on ultracold molecular collisions [45–47]. Avdeenkov and Bohn investigated the effect of external fields on ultracold collisions between OH or OD molecules [48-50]. Ticknor and Bohn [51] also studied OH-OH collisions in the presence of a magnetic field. They showed that magnetic fields of several thousand gauss suppress inelastic collision rates by about two orders of magnitude. In a recent study [33], we reported quantum dynamics calculations of reaction (1) for T =10-600 K and found no significant decrease of the rate coefficient in the temperature range 39-10 K, in accordance with conclusions of a recent experimental study by Carty et al. [52]. Our calculations for reaction probabilities were in excellent agreement with those of Xu et al. [53] for collision energies $E_c > 0.012$ eV.

In this paper, we present the quantum dynamics of reaction (1) at low and ultralow collision energies to explore the behavior of complex-forming chemical reactions at cold and ultracold temperatures. Since OH molecules have been experimentally cooled and trapped at low temperatures, we believe that collisional properties of the O+OH reaction will be of considerable interest to the cooling and trapping community. The paper is organized as follows: The details of the quantum mechanical formalism along with convergence tests are discussed in Sec. II. Results of cross sections, rate coefficients, and state-to-state product distributions are given in Sec. III. We also include in this section a discussion on the usefulness of a classical model in describing cold collisions of O and OH. Conclusions are presented in Sec. IV.

II. METHODOLOGY

A. Potential energy surfaces

We employed a modified version of the electronically adiabatic ground state $(1 \ ^2A'')$ potential energy surface (PES) of HO₂ calculated by Kendrick and Pack [55] using a diatomics-in-molecule (DIM) formalism. This new version includes improvements to the long-range behavior and is referred to as the DIMKP PES. In particular, a switching function was implemented which more smoothly turns on the long-range van der Waals potentials for the electronic ground states of both O₂ and OH. This switching function is given by $f_{\text{switch}}=0.5\{\tanh[\alpha(r-r_0)]+1\}$ where $\alpha=1$, $r_0=7.0a_0$ for $O_2({}^{3}\Sigma_{a}^{-})$ and $r_0=10a_0$ for $OH({}^{2}\Pi)$. A minor global refitting of the DIM HO₂ PES to the original set of ab initio data was required in order to account for the new switching functions and ensure a smooth transition to the long-range behavior. The same long-range coefficients were used as in the original version of the surface, for OH(²II), $C_6^{\text{O-H}} = 9.295 E_h a_0^6$, $C_8^{\text{O-H}} = 169.09 E_h a_0^8$, $C_{10}^{\text{O-H}} = 4060.85 E_h a_0^{10}$, and for $O_2({}^3\Sigma_g^{-})$, $C_6^{\text{O-O}} = 14.89 E_h a_0^6$, $C_8^{\text{O-O}} = 206.67 E_h a_0^8$, and $C_{10}^{\text{O-O}} = 3753.745 E_h a_0^{10}$ [55]. The global fit in the interaction region is essentially identical to the original fit with nearly the same rms deviation of 0.099 eV (2.3 kcal/mol). The improvements to the long-range behavior are important for the ultracold collisions studied in this work but should not significantly affect the



FIG. 1. Potential energy curves for the three lowest ${}^{2}A''$ states of HO₂ for the DIMKP PES, for an O-HO linear approach with $r_{\rm OH} = 1.83a_0$. The conical intersections arising at $R_{\rm O-HO} \approx 10.8a_0$ is shown in the inset.

results of previous scattering calculations at higher (thermal) energies [56]. We present in Fig. 1 the potential energy curves for the three lowest ${}^{2}A''$ states of HO₂ for the DIMKP PES, for an O-HO linear approach. We also note in the inset of Fig. 1 that the DIMKP PES predicts a shallow conical intersection along the O-HO approach due to the crossing of the OH(Π) and OH(Σ) states. For a fixed $r_{OH}=1.83a_0$, this crossing occurs at $R_{O-HO} = 10.8235a_0$ and its energy lies $8.30 \times 10^{-4} \text{ eV}$ ($\approx 9.6 \text{ K}$) below the asymptotic energy of the O+OH channel. For comparison purposes, we also employed the ab initio PES computed by Xu, Xie, Zhang, Lin, and Guo [57,58], referred to as the XXZLG PES. The XX-ZLG PES has been used in a number of quantum dynamics calculations of the O+OH system at high collision energies [53,54,59]. The present DIMKP PES was employed for the first time for this reaction in our previous work [33] and it is preferred at low energies as it includes accurate long-range coefficients.

B. Quantum mechanical approach and convergence tests

The quantum dynamics calculations have been performed using the adiabatically adjusting principal-axis hyperspherical approach of Pack and Parker [60]. The method uses the democratic Smith-Whitten hyperspherical coordinates in the inner region ($\rho < 17a_0$) that includes the triatomic well of the HO₂ system and the Delves-Fock hyperspherical coordinates in the outer region ($\rho > 17a_0$) in the valleys of the H+O₂ and O+OH arrangement channels. For given values of the total angular momentum quantum number J and hyperspherical radius ρ , the wave function is expanded onto a basis set of adiabatic functions, which are eigenfunctions of a triatomic hyperangular Hamiltonian. A hybrid DVR-FBR (discrete variable representation-finite basis representation) primitive basis set [61] combined with an Implicitly Restarted Lanczos algorithm is used to diagonalize the hyperangular Hamiltonian matrix. The time-independent Schrödinger equation yields a set of differential close-coupling equations in ρ ,

TABLE I. Convergence of the elastic cross section $\sigma_{el}^{J=0}$ in units of 10^{-13} cm² molecule⁻¹ with the matching distance ρ_m for O +OH(v=0, j=0) using the DIMKP PES, for n=393.

	$\frac{\sigma_{\rm el}^{J=0}}{\rho_m \left(a_0\right)}$				
E_c (eV)	26.8	32.7	39.9	44.0	
10 ⁻¹⁰	0.4995	0.5019	0.4786	0.4679	
10-9	0.4965	0.4977	0.4742	0.4635	
10 ⁻⁸	0.4877	0.4853	0.4610	0.4505	
10 ⁻⁷	0.4596	0.4472	0.4206	0.4110	
10-6	0.3708	0.3369	0.3085	0.3021	
10 ⁻⁵	0.1432	0.1164	0.1108	0.1123	
10 ⁻⁴	0.005536	0.005214	0.005300	0.005217	
10 ⁻³	0.001531	0.001516	0.001506	0.001507	

which are solved using the log-derivative matrix propagation method of Johnson [62]. The log-derivative matrix is propagated to a matching distance (ρ_m) where asymptotic boundary conditions are applied to evaluate the reactance matrix K^J and the scattering matrix S^J . The square elements of the S^J matrix provide the state-to-state transition probabilities P^J . The matching distance and all other parameters employed in the calculations were determined by optimization and extensive convergence studies. To secure convergence of the reaction probabilities, the number of hyperspherical channels, n, included in the close coupling equations is 393. This is sufficient to obtain converged results at low and ultralow energies. The cross sections are calculated using the standard formulas

$$\sigma_{\rm el}^{J} = \frac{\pi}{{\rm k}^2} |1 - S_{ii}^{J}|^2, \quad \sigma_{\rm re}^{J} = \frac{\pi}{{\rm k}^2} \sum_{{\rm reactive } j} |S_{ij}^{J}|^2,$$

where *i*, *j* denote initial and final quantum states. The nonthermal elastic and reactive rate coefficients are given by $\sigma_{\rm el}\nu$ and $\sigma_{\rm re}\nu$ where $\nu = \hbar k/\mu$ is the incident velocity for relative motion of the O atom and the OH molecule.

The convergence of the elastic cross section $\sigma_{el}^{J=0}$ and the nonthermal reactive rate coefficient $\sigma_{re}^{J=0}\nu$ are presented in Tables I and II for O+OH(v=0, j=0) collisions on the DIMKP PES. At vanishing collision energies, these quantities attain finite values as required by the Bethe-Wigner laws [63,64]:

$$\sigma_{\rm el}^{I=0} \rightarrow {\rm const}, \quad \sigma_{\rm re}^{I=0} \times \nu \rightarrow {\rm const}.$$

The tables also show convergence of the results with the matching distances. At low energies the elastic cross section converges less rapidly with the matching distance ρ_m than the reactive one. This is because the long-range contribution to the interaction potential is not negligible compared to the kinetic energy in the entrance channel, even for moderately large values of the hyperradius. Thus, elastic cross sections are generally more sensitive to the long-range tail of the interaction potential. For the parameters in Tables I and II the reactive rate coefficients are converged to within 1% while

TABLE II. Convergence of the nonthermal reactive rate coefficients $\sigma_{re}^{J=0}\nu$ in units of 10^{-10} cm³ molecule⁻¹ s⁻¹ with the matching distance ρ_m for O+OH(v=0, j=0) using the DIMKP PES, for n = 393.

	$\sigma_{ m re}^{J=0} u$				
	$ ho_m(a_0)$				
E_c (eV)	26.8	32.7	39.9	44.0	
10 ⁻¹⁰	0.1965	0.2777	0.3123	0.3133	
10 ⁻⁹	0.1954	0.2755	0.3095	0.3104	
10 ⁻⁸	0.1920	0.2688	0.3010	0.3018	
10^{-7}	0.1819	0.2490	0.2760	0.2765	
10 ⁻⁶	0.1544	0.1979	0.2123	0.2119	
10^{-5}	0.09835	0.1080	0.1080	0.1073	
10^{-4}	0.03748	0.03713	0.03724	0.03714	
10 ⁻³	0.008704	0.008745	0.008761	0.008765	

the elastic cross sections are converged within 3%. All of the final results presented here are obtained using $\rho_m = 44.0a_0$, which is especially necessary to get converged results at $E_c < 10^{-4}$ eV [65].

III. RESULTS AND DISCUSSION

A. Cross sections and rate coefficients

The J=0 elastic and reactive cross sections are plotted as a function of the collision energy in Fig. 2 for the DIMKP PES. The corresponding nonthermal rate coefficients are presented in Fig. 3. In both figures, the Bethe-Wigner laws are satisfied at ultralow collision energies. The elastic cross section and the reactive rate coefficient converge to values of 4.6×10^{-14} cm² molecule⁻¹ and 3.1 $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, respectively, in the limit of zero energy. The elastic rate coefficient and the reactive cross section behave, respectively, as the square root and the inverse



FIG. 2. (Color online) J=0 cross section as a function of the collision energy for the elastic [red (gray) curve], inelastic (green dashed curve), and reactive (black curve) collisions of O atoms with OH(v=0, j=0) molecules for the DIMKP PES.



FIG. 3. (Color online) J=0 nonthermal rate coefficient as a function of the collision energy for the elastic [red (gray) curve], inelastic (green dashed curve), and reactive (black curve) collisions of O atoms with OH(v=0, j=0) molecules for the DIMKP PES.

of the square root of the collision energy. The Bethe-Wigner regime is reached at $E_c \approx 10^{-4}$ K, where the reactive rate coefficient is about one order of magnitude higher than that of the elastic counterpart. At $E_c = 10^{-6}$ K the reactive rate coefficient is two orders of magnitude larger than the elastic one. This is reminiscent of other exothermic barrierless systems such as alkali-metal atom-diatom collisions [21–29]. At energies between $E_c = 0.01$ and 30 K, elastic and reactive rate coefficients are of comparable magnitude. For $E_c > 30$ K, the elastic scattering is more efficient than reactive scattering. The inelastic rotational excitation to the j=1 level opens up at $E_c=52$ K and its cross section is comparable to the reactive contribution.

The J=0 contribution to the elastic, inelastic and reactive rate coefficients evaluated using the XXZLG PES are presented in Fig. 4 as functions of the collision energy. For E_c >1 K, all three rate coefficients are of comparable magnitudes with those obtained from the DIMKP PES. For E_c <1 K, the reactive rate coefficient is about two orders of magnitude smaller than that obtained using the DIMKP PES. The differences can be traced to the incomplete description



FIG. 4. (Color online) Same as Fig. 3 but for the XXZLG PES.



FIG. 5. Vibrational populations of the product O₂ molecule in O+OH(v=0, j=0) \rightarrow H+O₂(v_f) reaction evaluated using the DIMKP PES at a collision energy of 10⁻⁶ K and J=0.

of the long-range interaction potential in the XXZLG PES. It does not properly include the long-range potential in the O +OH channel as it was not designed for quantum dynamics calculations at ultralow energies. Thus, the comparison of the results obtained using the two surfaces highlights the crucial role of the long-range interaction potential in chemical reaction dynamics at low temperatures. The importance of the long-range intermolecular forces in the O-OH system in determining its rate coefficient has been pointed out by Clary and Werner [66]. In the following, we restrict our calculations to the DIMKP PES.

The vibrational populations of molecular oxygen formed in O+OH(v=0, j=0) collisions, evaluated using the DIMKP PES at an energy of 10⁻⁶ K and J=0 are presented in Fig. 5. Oxygen molecules are predominantly formed in vibrational levels $v_f=(0-2)$ with a slight preference for the ground vibrational state $v_f=0$. Thus, a significant fraction of the O₂ molecules formed is in excited vibrational states. The rotational level distributions of molecular oxygen formed in O +OH(v=0, j=0) collisions for J=0 are presented in Fig. 6 for each final vibrational level v_f populated by the reaction at an energy of 10⁻⁶ K. The results show that low rotational levels are generally preferred for each of the final vibrational levels. Since the incident channel includes only the *s* wave, the final rotational distribution is largely determined by the anisotropy of the interaction potential.

Explicit calculations of rate coefficients would require reaction probabilities for all contributing values of the total angular momentum quantum number *J*. This is a computationally demanding problem for the O+OH reaction if full quantum dynamics calculations are employed, especially when many *J* values contribute to the reaction probability. The *J*-shifting approximation [67] is widely used to compute rate coefficients when full quantum calculations are not practical. This is a good approximation for barrier reactions which involve a transition state but not for complex-forming reactions. Nevertheless, the *J*-shifting approximation has been applied to the O+OH reaction in a number of previous studies [33,53,68–70] and it has been demonstrated that it can predict rate coefficients within about 40% of numerically exact calculations [54]. Here we use the *J*-shifting approxi-



FIG. 6. Rotational populations of the product O₂ molecule in O+OH(v=0, j=0) \rightarrow H+O₂($v_f=0, 1, 2, 3, j_f$) reaction evaluated using the DIMKP PES at a collision energy of 10⁻⁶ K and J=0.

mation [67] to compute the rate coefficients for the O+OH reaction. The rate coefficient is given by the expression

$$k_{v,j}(T) = \frac{1}{2\pi\hbar Q_{\rm R}} \left(\sum_{J} (2J+1)e^{-E_{\rm shift}^{J}/(k_{B}T)} \right) \\ \times \int_{0}^{\infty} P_{v,j}^{\rm re,J=0}(E_{c})e^{-E_{c}^{J}(k_{B}T)}dE_{c},$$
(2)

where k_B is the Boltzmann constant, $P_{v,j}^{\text{re},J=0}$ is the J=0 reaction probability, and E_{shift}^J is the height of the effective barrier for a given partial wave J in the entrance channel. To determine the barrier height for a given partial wave, we first evaluate the effective potential V_{eff}^J :

$$V_{\rm eff}^{J} = \frac{\hbar^2 J(J+1)}{2\mu (R_{\rm O-OH})^2} + V_{\rm min}(R_{\rm O-OH}), \qquad (3)$$

where $V_{\min}(R_{\text{O-OH}})$ is the minimum energy path of the reaction as a function of the atom-molecule center-of-mass separation, $R_{\text{O-OH}}$, and μ is the reduced mass of the O-OH system. In Eq. (2), $Q_R = Q_{\text{trans}}Q_{\text{el}}$ is the reactant partition function. For the translational partition function we used the standard formula, $Q_{\text{trans}} = (\mu k_B T / 2 \pi \hbar^2)^{3/2}$. For the electronic partition function we used the expression given by Graff and Wagner [71],

$$Q_{\rm el} = \frac{(5+3e^{-228/T}+e^{-326/T})(2+2e^{-205/T})}{2}.$$

The effective barriers V_{eff}^J for the DIMKP PES are shown in Fig. 7 for J = [0-200; 10]. As Fig. 7 illustrates, the "reef" visible in the effective potential at $R_{\text{O-OH}} = 5a_0$ for low values of J becomes an effective barrier for $J \ge 70$ as indicated by the bold line. The barrier heights E_{shift}^J and their locations R_{shift}^J are reported in Table III for J = (1-10).



FIG. 7. Effective potentials V_{eff}^J as functions of $R_{\text{O-OH}}$ for J = [0-200;10] for the DIMKP PES. The bold line corresponds to J=70.

The elastic, inelastic, and reactive rate coefficients of the O+OH(v=0, j=0) reaction evaluated using the J-shifting method for the DIMKP PES are shown in Fig. 8 for T $=10^{-6}-10^{3}$ K. As indicated earlier, the Bethe-Wigner regime is reached for temperatures below $T \approx E_c \approx 10^{-4}$ K. The value of the rate coefficient in the zero-energy limit is 6.2 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. This is a factor of 5 smaller than the rate coefficient reported as $\sigma_{re}^{J=0}\nu$ in Fig. 3. The difference comes from the electronic partition function in the denominator in Eq. (2), which is equal to 5 as $T \rightarrow 0$. In experiments using the Stark decelerator methods, OH molecules were cooled to T=10-100 mK. In this temperature range, our computed values of the elastic rate coefficients are comparable to the reactive ones and will not favor sympathetic cooling of OH by collisions with O atoms. Similar conclusions have been found by Lara et al. [43,44] for collisions between OH molecules with Rb atoms. The relatively large rate coefficient for the reaction in the zero-temperature limit indicates that barrierless exothermic reactions occur at significant rates at ultracold temperatures, in agreement with similar results for alkali-metal atom-diatom reactions [21–29]. Figure 8 shows that the minimum value of the rate

TABLE III. Comparison of the heights and positions of the effective barriers between the *J*-shifting approximation and the Langevin model.

J	$egin{array}{c} E^J_{ m shift}\ ({ m K}) \end{array}$	$\begin{array}{c} R_{\rm shift}^J \\ ({\rm units of } a_0) \end{array}$	$E_{ m Lang}^{J}$ (K)	$\begin{array}{c} R_{\text{Lang}}^{J} \\ (\text{units of } a_{0}) \end{array}$
1	0.022	25.4	0.022	25.4
2	0.11	19.3	0.11	19.3
3	0.30	18.6	0.32	16.3
4	0.54	18.4	0.68	14.3
5	0.86	18.0	1.26	12.9
6	1.26	17.5	2.08	11.9
7	1.75	17.1	3.20	11.1
8	2.34	16.7	4.68	10.4
9	3.04	16.4	6.53	9.8
10	3.84	16.1	8.83	9.3

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FIG. 8. (Color online) Rate coefficients for the elastic [red (gray) curve], inelastic (green dashed curve), and reactive (black curve) scattering in O+OH(v=0, j=0) collisions evaluated using the DIMKP PES. The rate coefficient from a classical Langevin model (black dashed curve) is also shown (see text for detail).

coefficient for the O+OH reaction is about 4.9 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at $T=5 \times 10^{-3}$ K. This provides a lower limit for O₂ formation by reaction (1). We note that the inelastic process becomes more probable than the reactive process for T>330 K.

B. Classical capture model

We shall now compare our quantum dynamics results with a classical capture model also known as the Langevin model [72]. This model has been shown to work quite well for a certain range of collision energy, for atom-exchange reactions such as K+K₂ [23] and Li+Li₂ [24], and also for nonreactive Rb+OH collisions [43,44]. We have shown [31] that the Langevin model predicts rate coefficients in close agreement with experimental values for Rb+Rb₂ [8], Cs +Cs₂ [10,11], and Rb or Cs+RbCs [13] collisions reported recently. For the O+OH reaction, Clary and Werner [66] used an adiabatic capture theory [73], while Davidsson and Nyman [74] used a generalized Langevin model. Both studies showed good agreement between theoretical and experimental rate coefficients. Here we test the validity of the Langevin model against a time-independent quantum formalism and J-shifting method for the O+OH reaction. For a nonrotating diatomic molecule (j=0) at large atom-molecule separations R_{O-OH} , for a given value of J, the interaction potential can be approximated by an effective potential V_{Lang}^{J} , composed of a repulsive centrifugal term and an attractive van der Waals term:

$$V_{\text{Lang}}^{J} = \frac{\hbar^2 J (J+1)}{2 \mu (R_{\text{O-OH}})^2} - \frac{C_6^{\text{O-OH}}}{(R_{\text{O-OH}})^6}.$$

At an atom-diatom distance of

$$R_{\text{Lang}}^{J} = \left(\frac{6\mu C_{6}^{\text{O-OH}}}{\hbar^{2} J(J+1)}\right)^{1/4},$$

the height of the effective potential is given by:

$$E_{\text{Lang}}^{J} = \frac{2}{3\sqrt{3}} (C_{6}^{\text{O-OH}})^{-1/2} \left(\frac{\hbar^{2} J(J+1)}{2\mu}\right)^{3/2}$$

The quantities E_{Lang}^{J} and R_{Lang}^{J} are reported in Table III for J=1-10. The C_{6}^{O-OH} coefficient is evaluated by fitting the long-range part of the minimum energy path $V_{\min}(R_{O-OH})$. This yields a value of $C_6^{O-OH} \approx 9.2E_h a_0^6$, which is much smaller than the sum of the atom-atom coefficients C_6^{O-H} $+C_6^{\text{O-O}}=24.2E_ha_0^6$. In the DIM model, the smaller $C_6^{\text{O-OH}}$ coefficient is due to the presence of significant diatomic mixing in the OH diatomic states for $r_{OH} = 1.83a_0$ [see, for example, Eqs. (34)-(37) in Ref. [55]]. This mixing gives rise to an effective C_6 coefficient of the O-HO approach of $\alpha_1 C_6^{\text{O-H}}$ $+\alpha_2 C_6^{\text{O-O}} = 9.2 E_h a_0^6$, where the multiplicative constants α_1 and α_2 depend on the level of diatomic mixing. As $r_{\rm OH}$ increases, the diatomic mixing decreases and $\alpha_1 \rightarrow 1$ and $\alpha_2 \rightarrow 1$. The dependence of the long-range coefficients for atom-diatom interactions on the diatomic separation has also been noted and investigated in recent work on the Li+Li₂ and Na+Na₂ systems [75,76]. For the atom-molecule reduced mass we used $\mu = 15023.74$ a.u. In the Langevin model, the rate coefficient as a function of the temperature is given by the expression

$$k_{\rm Lang}(T) = \frac{\pi}{Q_{\rm el}} \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \left(\frac{2C_6^{\rm O-OH}}{k_B T}\right)^{1/3} \Gamma(2/3).$$

The rate coefficient predicted by the Langevin model is plotted in Fig. 8 (black dashed curve). Except in the Bethe-Wigner regime for $T < 10^{-4}$ K, where the classical model is not valid, the Langevin model predicts rate coefficients in semiquantitative agreement with those obtained from the quantum calculations. Overall, the reactive rate coefficients oscillate slightly around the Langevin line, as in other barrierless systems such as $K+K_2$ [23] and $Li+Li_2$ [24]. However, the Langevin model yields good agreement only for a restricted range of temperatures. The lower limit of the model prediction is restricted by the number of partial waves included in the calculations. In previous studies [23,24], it has been found that when four (J=0-3) or more partial waves are included, the quantum and classical results are in good agreement. If fewer than four partial waves are involved, the quantum character becomes dominant and the results cannot be compared with the classical model. These previous studies have also shown that the maximum of the quenching rate coefficient for a given partial wave J occurs at about a collision energy comparable to the height of the barrier, E_{Lang}^{J} . Thus, the lower limit corresponds to a collision energy of $E_{\text{Lang}}^{J=3}$ =0.32 K (see Table III) for the present system. The upper limit is bounded by the long-range part of the potential. When the Langevin radius R'_{Lang} is located at a distance where the long-range part of the potential is not described by the van der Waals interaction, E_{Lang}^{J} will differ from E_{shift}^{J} . In this case, the classical results will differ from the quantum calculations. Table III shows that this is the case for J=3, and the upper limit of the model also corresponds to a collision energy of $E_{\text{Lang}}^{J=3}=0.32$ K. Thus, the Langevin model gives quantitative agreement for temperatures around $T \approx 0.3$ K, as seen in Fig. 8. For T > 0.3 K, the rate coefficient depends on the exact details of the effective potential in the entrance channel. However, the classical result is in overall agreement with the quantum result, although the classical model predicts a smaller value for the rate coefficient. This is because $E_{\text{shift}}^J < E_{\text{Lang}}^J$ for J > 3 (see Table III) and it is less probable for reactivity to occur with the Langevin model. Therefore, the Langevin model provides a lower limit of the rate coefficients for T=1-100 K which affirms the theoretical conclusions of Ref. [33] and experimental conclusions of Ref. [52], that the rate coefficient of reaction (1) is unlikely to vanish for T<10 K. We also note that the Langevin rate coefficient is in semiquantitative agreement with the inelastic rate coefficient in the range T=100-1000 K. The difference is less than 30%.

IV. CONCLUSION

This paper presents a quantum mechanical investigation of an ultracold barrierless reaction with chemically distinct reactants and products. We investigated dynamics of molecular oxygen formation in ultracold collisions of the hydroxyl radical and atomic oxygen using a time-independent quantum mechanical method based on hyperspherical coordinates. It has been found that formation of molecular oxygen occurs with a relatively large rate coefficient of 6.2 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at ultracold temperatures. The oxygen molecules are mainly formed in the v=0-2 vibrational levels with a slight preference for the v=0 level. Calculations show that at temperatures of T=10-100 mK, the elastic cross sections are not large enough to achieve efficient evaporative cooling in collisions between OH molecules and O atoms. We predict a lower limit of 4.9 $\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for the rate coefficient for the O+OH(v=0, j=0) reaction at $T=5 \times 10^{-3}$ K. This shows that formation of O₂ molecules is significant even at ultracold temperatures. It has been found that a classical capture model is valid for temperatures around $T\approx 0.3$ K where quantum and classical calculations yield comparable results. Based on our analysis of the long-range interaction potential we find that for T=1-10 K the Langevin model can provide a lower limit to the quantum reactive rate coefficients calculated within the J-shifting approximation.

Future work will consider the effects of the geometric phase and nonadiabatic couplings between different PESs of HO_2 on the reaction dynamics. The geometric phase due to the conical intersection of two PESs may have an important effect at low and ultralow collision energies where only a few partial waves contribute to the reaction probabilities.

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