

Dynamics Study of the $O_2(v) + HO_2$ Atmospheric Reaction

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A quasiclassical trajectory study of the title five-atom reaction is reported for vibrational states of O_2 over the range of $12 \leq v \leq 27$ using a realistic double many body expansion potential energy surface recently reported for $HO_4(^2A)$. The results indicate that it can be a potential source of ozone in the upper atmosphere.

1. Introduction

Vibrationally excited molecules can play a significant role in chemical reactions due to their unique and interesting chemical and physical properties. Examples of common and naturally occurring processes that lead to the formation of vibrationally excited molecules are exothermic chemical reactions, ultraviolet photodissociation, and electrical discharges. In fact, with the further development of stimulated emission pumping^{1–9} and overtone pumping,^{10–17} investigation of collisional properties of vibrationally hot molecules has blossomed. Moreover, for vibrationally excited diatomic species, fully quantum-state-resolved experiments are possible and quantum mechanical identification of all excited states is unambiguous. The vibrational dependence of the collision dynamics involving diatomics is therefore an intriguing topic since it offers an understandable bridge between low and high vibrational excitation.¹⁸

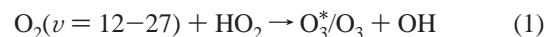
Vibrationally excited molecular oxygen (hereafter denoted by $O_2(v)$) can be formed with significant efficiency in the photodissociation of O_3 at¹⁹ 248 and²⁰ 226 nm in states as high as $v = 27$. This vibrationally excited $O_2(^3\Sigma_g^-)$ has recently been proposed^{6,20–22} to explain the limitations of atmospheric ozone models.^{23–25} Indeed, although questionable,²⁶ there has been a long-standing problem with ozone models for the upper stratosphere and mesosphere that underpredict the measured ozone concentrations,²⁵ with the above unexpected ozone source being viewed as a possible explanation for the discrepancy. Such an “ozone deficit” problem has also prompted much effort to identify new sources of ozone.^{6,27–34}

Once produced, highly vibrationally excited species either fluoresce or undergo deactivation in collisions with ambient molecules such as O_2 , O_3 , OH , N_2 , CO_2 , and N_2O . Over the past decade, both experimental and theoretical progress has been made in measuring the vibrational level dependence of the total removal rate constants in collisional processes.^{6,18,19,21,27,28,30–36} However, remarkably absent from this progress list is HO_2 , which is an important natural species of the atmosphere. In fact, the HO_2 radical is a key intermediate for many chemical reactions such as those involved in atmospheric chemistry,^{37–44} stratospheric formation and destruction of ozone,^{45–47} and photochemical air pollution.^{48–52} An investigation of the collisional properties of highly vibrationally excited O_2 with HO_2 radicals is therefore of great interest.

Until recently, no single theoretical study of the $O_2(v) + HO_2$ reaction had been reported in the literature. Such a lack of

theoretical work can only be attributed to difficulties in calculating a reliable $HO_4(^2A)$ potential energy surface. On the basis of previous work,^{53–58} we have developed⁵⁹ such a realistic surface by using the double many body expansion^{60,61} (DMBE) method as implemented for single-valued functions. Moreover, we have used^{59,62,63} this HO_4 DMBE surface to study the reaction $OH(v) + O_3 \rightarrow HO_2 + O_2$. For the states $v = 0$ and 9, good agreement has been found with the data recommended by the IUPAC subcommittee on gas kinetics data evaluation for atmospheric chemistry⁶⁴ and the measurements of Greenblatt and Wiesenfeld,⁶⁵ respectively. In turn, for $1 \leq v \leq 8$, there is essentially no experimental data, and hence a comparison with available results on the $OH(v)$ quenching based on nonreactive collisions has been presented. The results indicate that vibrational excitation strongly enhances reactivity, with removal of vibrationally excited OH occurring predominantly through chemical reaction. Thus, such a work paved the way to investigate the dynamics and kinetics of the $O_2(v) + HO_2$ reaction for high v states that as shown below, may be a potential source of ozone in the upper atmosphere.

A major goal of the present work is to report a detailed study of the reaction



where the star indicates that the formed ozone molecules have an internal energy above the dissociation limit. Thus, they will ultimately decompose through the unimolecular dissociation reaction



or will stabilize in the presence of some inert species (M) through the reaction



For the dynamics calculations, we will employ (as in previous work^{59,62,63}) the quasiclassical trajectory (QCT) method and the $HO_4(^2A)$ DMBE potential energy surface; throughout the paper, the absence of a specific vibrational state in a reactant species implies that it is in the ground vibrational state (e.g., $HO_2 \equiv HO_2(v_1 = 0, v_2 = 0, v_3 = 0)$, where v_1 is the quantum number for the symmetric stretching vibrational normal mode, v_2 is for the bending normal mode, and v_3 is for the asymmetric stretching normal mode). The paper is organized as follows. Section 2 provides a brief survey of the $HO_4(^2A)$ DMBE

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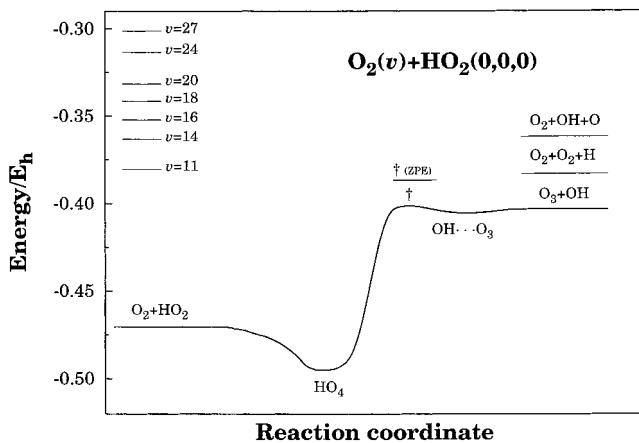


Figure 1. Minimum energy path for formation of $O_3^*/O_3 + OH$. The saddle point geometry is indicated by the symbol †. Also shown are the energies of $O_2(v = 11 - 27) + HO_2$, $O_2 + O_2 + H$, and $O_2 + OH + O$.

potential energy surface, while the computational method is described in section 3. The dynamics results are presented and discussed in section 4, while the major conclusions are in section 5.

2. Potential Energy Surface

All calculations reported in this work have employed a full-dimensional (9D) DMBE potential energy surface⁵⁹ for the ground electronic state of HO_4 . Because its topography has been illustrated elsewhere,^{59,62,63} we report in Figure 1 only the minimum energy path for the title reaction and some energetic features that are of relevance for the present work. These refer to the energetics of the $O_2(v = 12-27) + HO_2$ channels and relevant product ones. Note that for $v = 11$, the reactive channel leading to ozone formation is just barely open. However, for vibrational states $v \geq 16$, all reactive channels ($O_3^*/O_3 + OH$, $O_2 + O_2 + H$, and $O_2 + OH + O$) are accessible over the complete range of translational energies.

3. Computational Procedures

Following previous work,^{59,62,63} we have used the QCT method in the present study of the $O_2(v) + HO_2$ reaction. To run the classical trajectories, we have utilized extensively adapted versions of the MERCURY/VENUS96⁶⁶ codes, which accommodate the HO_4 DMBE potential energy surface and make the appropriate assignment of the relevant reactive channels described in section 2. Calculations have been carried out for diatom-triatom translational energies over the range of $1.0 \leq E_{tr}/\text{kcal mol}^{-1} \leq 20$, as specified in Table 1. In all cases, the initial rotational quantum number of the colliding O_2 molecule has been fixed at the ground level ($j = 1$). Although the most populated rotational level in a Boltzmann distribution at a typical stratospheric temperature of 150 K is $j = 5$, we believe that such a constraint has no major effect on the conclusions to be drawn in the present work. This is tentatively elucidated by carrying out some calculations of the thermal rate coefficient using a thermally averaged j distribution. For this, we have selected the temperatures of $T = 150$ and 300 K, with the latter being chosen to define the rotational distribution of HO_2 in all calculations reported in this work when O_2 is kept in the $j = 1$ rotational state. In fact, the HO_2 molecule has then been considered in the ground vibrational state ($v_1 = 0, v_2 = 0,$

TABLE 1: Summary of Trajectory Calculations for $O_3^*/O_3 + OH$ Formation

v	E_{tr} (kcal mol ⁻¹)	$b_{max}(a_0)$	N_r^a	100 P_r	$\sigma^x \pm \Delta\sigma^x/a_0^2$
18	1.0	6.80 ^b	2	0.10	0.15 ± 0.11
	2.0	4.54	3	0.15	0.10 ± 0.06
	4.0	3.78	4	0.20	0.09 ± 0.05
	6.0	3.40	14	0.70	0.25 ± 0.07
	8.0	3.78	13	0.65	0.29 ± 0.08
20	1.0	9.83	9	0.45	1.37 ± 0.45
	2.0	8.31	16	0.80	1.74 ± 0.43
	4.0	7.18	17	0.85	1.38 ± 0.33
	6.0	6.43	20	1.00	1.30 ± 0.29
	8.0	6.80	21	1.05	1.53 ± 0.33
	12.0	7.56	21	1.05	1.88 ± 0.41
24	1.0	11.72	63	3.15	13.58 ± 1.68
	2.0	10.20	61	3.05	9.98 ± 1.26
	4.0	9.07	58	2.90	7.50 ± 0.97
	6.0	8.50	51	2.55	5.79 ± 0.80
27	1.0	12.09	101	5.05	23.21 ± 2.25
	2.0	10.39	99	4.95	16.80 ± 1.65
	4.0	9.26	97	4.85	13.06 ± 1.29
	6.0	8.88	82	4.10	10.16 ± 1.10
	8.0	8.88	79	3.95	9.79 ± 1.08
	12.0	8.50	70	3.50	7.95 ± 0.93

^a Number of reactive trajectories. ^b For convenience, the data in this and following tables is often reported with two significant figures, although this by no means implies that such an accuracy is always applicable, as it can be anticipated from the number of reactive events.

$v_3 = 0$) with its rotational energy being assigned by using the microcanonical sampling scheme for a temperature of 300 K. As the results reported below seem to indicate, such a choice should not have a drastic influence on the final results. An optimum step size for numerical integration of 1.5×10^{-16} s has been chosen, which warrants conservation of the total energy to better than 2 parts in 10^5 . In turn, the diatom-triatom initial separation has been fixed at $17a_0$ (a value sufficiently large to make the interaction negligible), while the maximum value of impact parameter (b_{max}) that leads to reaction has been estimated by computing batches of 200 trajectories for fixed values of b . This procedure allows an accuracy in b_{max} of $\pm 0.2a_0$ or so. Batches of at least 2000 trajectories have then been carried out for each translational energy making a total of about 8×10^4 trajectories. Such a number of trajectories is enough to yield reactive cross sections with an error smaller than about 10% for all translational energies considered in the current work.

For a specified translational energy, all relevant reactive cross sections and associated 68% uncertainties have been calculated. They will be denoted σ^x and $\Delta\sigma^x$, respectively, with x specifying the outcome $x = r$, total (this stands for formation of $O_3^*/O_3 + OH$, $O_2 + O_2 + H$, and $O_2 + OH + O$). From the cross sections, and assuming a Maxwell-Boltzmann distribution over the translational energy, the specific thermal rate coefficients are obtained as

$$k^x(T) = g_e(T) \left(\frac{2}{k_B T}\right)^{3/2} \left(\frac{1}{\pi\mu}\right)^{1/2} \int_0^\infty E_{tr} \sigma^x \exp\left(-\frac{E_{tr}}{k_B T}\right) dE_{tr} \quad (4)$$

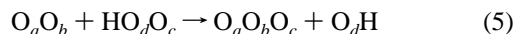
where $g_e(T) = 1/3$ is the electronic degeneracy factor that corresponds to the ratio of the electronic partition functions, k_B is the Boltzmann constant, μ is the reduced mass of the colliding particles, and T is the temperature.

TABLE 2: Summary of Trajectory Calculations That Led to Other Products

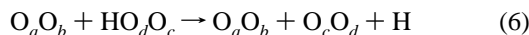
ν	E_{tr} (kcal mol ⁻¹)	O ₂ + O ₂ + H			O ₂ + OH + O		
		N_r	100P _r	$\sigma^r \pm \Delta\sigma^r/a_0^2$	N_r	100P _r	$\sigma^r \pm \Delta\sigma^r/a_0^2$
18	1.0				2	0.10	0.15 ± 0.10
	2.0	2	0.10	0.07 ± 0.05	2	0.10	0.07 ± 0.05
	4.0				3	0.15	0.07 ± 0.04
	6.0	1	0.05	0.02 ± 0.02	9	0.45	0.16 ± 0.05
	8.0	1	0.05	0.02 ± 0.02	10	0.50	0.22 ± 0.07
20	1.0	2	0.10	0.30 ± 0.21	19	0.95	2.88 ± 0.66
	2.0	1	0.05	0.11 ± 0.11	19	0.95	2.06 ± 0.47
	4.0	2	0.10	0.16 ± 0.11	27	1.35	2.19 ± 0.42
	6.0	1	0.05	0.07 ± 0.07	34	1.70	2.20 ± 0.37
	8.0	3	0.15	0.22 ± 0.13	37	1.85	2.69 ± 0.44
	12.0	2	0.10	0.18 ± 0.13	46	2.30	4.13 ± 0.60
24	1.0	9	0.45	1.94 ± 0.65	141	7.05	30.40 ± 2.47
	2.0	3	0.15	0.49 ± 0.28	166	8.30	27.15 ± 2.02
	4.0	4	0.20	0.52 ± 0.26	174	8.70	22.49 ± 1.37
	6.0	5	0.25	0.57 ± 0.25	186	9.30	21.13 ± 1.48
	8.0	5	0.25	0.57 ± 0.25	186	9.30	21.13 ± 1.48
	12.0	6	0.30	0.65 ± 0.27	210	10.50	22.81 ± 1.49
27	1.0	7	0.35	1.61 ± 0.61	284	14.20	65.25 ± 3.59
	2.0	7	0.35	1.19 ± 0.45	306	15.30	51.92 ± 2.73
	4.0	2	0.10	0.27 ± 0.19	326	16.30	43.91 ± 2.22
	6.0	4	0.20	0.50 ± 0.25	326	16.30	40.40 ± 2.05
	8.0	4	0.20	0.50 ± 0.25	330	16.50	40.89 ± 2.06
	12.0	7	0.35	0.80 ± 0.30	391	19.55	44.41 ± 2.01

4. Results and Discussion

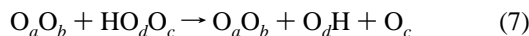
Tables 1 and 2 summarize the trajectory calculations carried out in the present work. Column one indicates the vibrational quantum number of the O₂ radical while the studied translational energies are given in column two. For these initial translational energies, the only open reactive channel for the formation of O₃^{*}/O₃ + OH is



where the indices *a*, *b*, *c*, and *d* label the four oxygen atoms (no consideration is made of different isomeric species; i.e., O_cO_aO_b, O_aO_cO_b, and O_aO_bO_c are treated jointly). Clearly, such a reaction refers to the formation of O₃^{*}/O₃ + OH products via an oxygen atom abstraction mechanism. As mentioned in section 2, there are additional reactive channels leading to O₂ + O₂ + H and O₂ + OH + O. For the case of O₂ + O₂ + H, the dominant channel is



In turn, for the products O₂ + OH + O, the open reactive channels are



In this case, the reactions in eqs 8 and 9 have identical probabilities of occurrence, with any differences being attributable only to statistical errors in the QCT calculations. However, as compared with such reactive channels, the reaction in eq 7 has a small probability. Note that the reactive probabilities for the formation of O₃^{*}/O₃ + OH and O₂ + OH + O increase with quantum number ν , while they only slightly increase for the formation of O₂ + O₂ + H. In summary, the dominant reactive channels for the title reaction are the formation of O₃^{*}/O₃ + OH

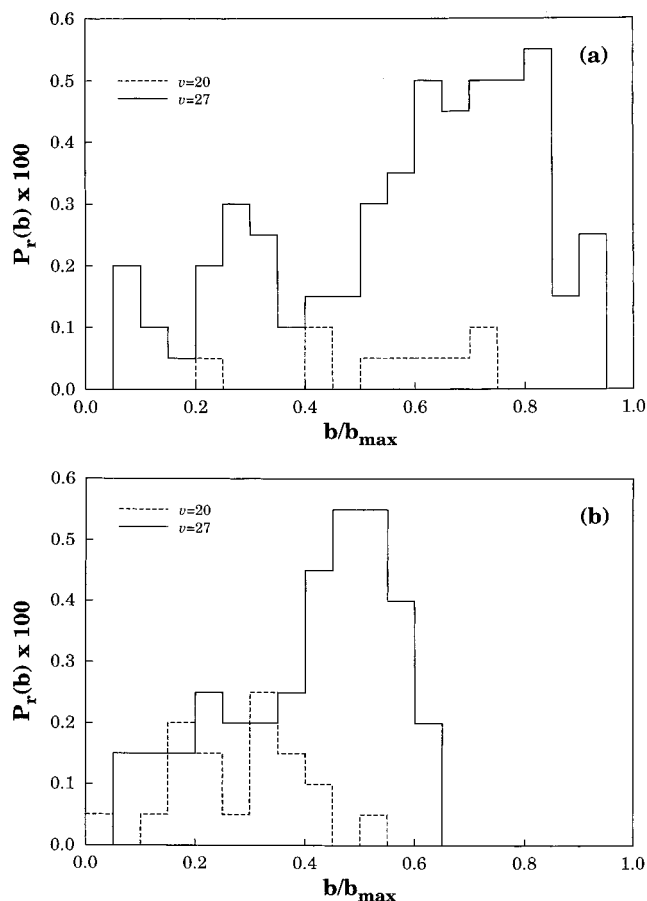


Figure 2. Opacity function for the formation of O₃^{*}/O₃: (a) capture type regime, $E_{tr} = 1$ kcal mol⁻¹; (b) barrier type regime, $E_{tr} = 12$ kcal mol⁻¹.

and O₂ + OH + O. For high ν states, the formation of O₂ + OH + O plays a role even more significant than O₃^{*}/O₃ + OH.

4.1. Dynamical Features. Table 1 shows the dependence of the maximum impact parameter with translational energy for the formation of O₃^{*}/O₃ + OH. As expected, the value of b_{max} increases with decreasing translational energy while for higher translational energies b_{max} is essentially constant or slightly increases with E_{tr} . Thus, we expect that reaction may occur via both “capture type” and “barrier type” mechanisms. Such a dependence of b_{max} on E_{tr} may be rationalized as follows. The dominant interactions between O₂ and HO₂ are, at large distances, of the quadrupole–dipole and quadrupole–quadrupole electrostatic types. Because the O₂ molecule is highly vibrationally excited (and this stretching leads to an increase of its electric quadrupole moment), one may then expect a more attractive long-range interaction for favorable orientations. A similar expectation holds for the dispersion forces. Thus, long-range forces may in part explain why b_{max} increases with decreasing translational energy. For high translational energies, such forces play a less important role, with an increase of translational energy leading to a small increase in b_{max} .

Figure 2 shows typical opacity functions (i.e., reactive probability vs impact parameter) for low (a) and high (b) translational energies and vibrational quantum numbers $\nu = 20$ and 27. For clarity, only the cases corresponding to $E_{tr} = 1$ and 12 kcal mol⁻¹ are shown in Figure 2. Note that the abscissae in these plots are b/b_{max} , with b_{max} being the largest impact parameter found in all batches that were run in the present work (12.09 a_0). The notable feature in Figure 2 is perhaps the fact that the opacity function shows two different patterns. For high

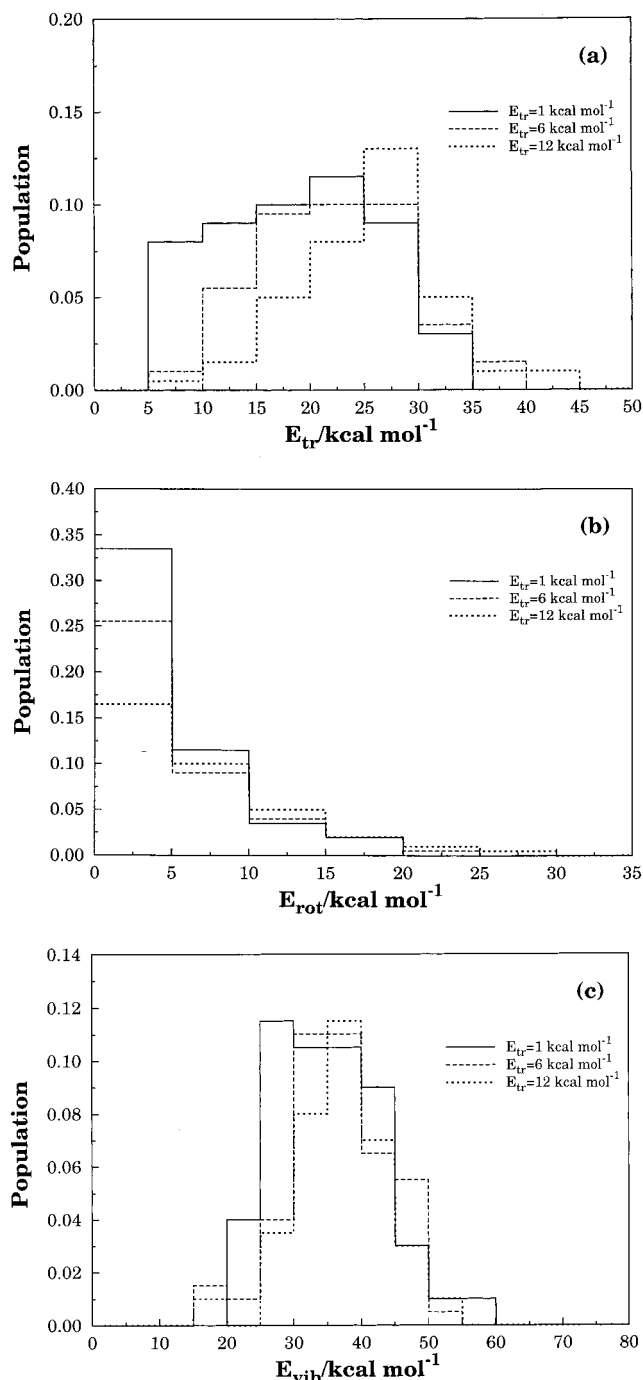


Figure 4. Energy distributions in the products for O_3^*/O_3 formation ($v = 27$): (a) translational, (b) rotational, and (c) vibrational energy.

the products. Also interesting is the fact that the percent translational energy plays a significant role, representing about 1/3 of the total energy of the products. This may be rationalized by noting that for direct reactions on a repulsive surface, one may expect from Polanyi's rules (the saddle point occurs late in the products valley) that vibrational energy in the reactants can be efficiently converted into translational energy of the products. Note also that the average vibrational energy of the product O_3^*/O_3 species is much higher than the corresponding zero-point energy⁶⁷ (ZPE) of 4.2 kcal mol⁻¹. Thus, for practical purposes, we may safely ignore in the present study the problem of ZPE leakage. Of course, no consideration is being given to the vibrational energy content of the other product molecule; for a detailed discussion of this issue in the context of the $\text{OH}(v) + \text{O}_3$ reaction, see ref 62.

Figure 5 shows the vibrational–rotational distribution of O_3^*/O_3 for the $\text{O}_2(v = 27) + \text{HO}_2$ reaction at two distinct energies (1 and 8 kcal mol⁻¹). Despite some scattering, it is possible to assign a relatively narrow range of internal energies to the O_3^* complexes for $E_{tr} = 1$ kcal mol⁻¹. The dotted line indicates the threshold energy for the dissociation of O_3^* into $\text{O}_2 + \text{O}$, while in dash are the lines corresponding to constant averaged internal energies, $\langle E_{vib} + E_{rot} \rangle$. Clearly, in both cases, most points lie above the dissociation threshold, which implies that the dominant product ozone molecules are energized species.

4.3. Dissociation Reaction $\text{O}_3^* \rightarrow \text{O}_2 + \text{O}$. We now discuss the dynamics of the energized O_3^* complexes, which carry an internal energy above the threshold for $\text{O}_2 + \text{O}$ dissociation. For this, once an O_3^* complex has been formed, we have allowed the trajectory to continue until dissociation. Figure 6 shows the logarithm of the decay rate of the O_3^* complexes as a function of time. It is seen that after some induction time, the rate of decay is roughly exponential with the concave curvature possibly being due to the fact that the ensembles of trajectories deviate from genuine microcanonical ones. Such a result suggests a RRKM type behavior, implying that efficient randomization of energy occurs among the various degrees of freedom. Thus, after some induction time, the energy contained in specific vibrational modes is promptly pumped to those modes that are coupled to the reaction path leading to dissociation. Such an observation is similar to that reported elsewhere²⁷ for the O_3^* complexes formed in the $\text{O}_2(v') + \text{O}_2(v'')$ reaction.

4.4. Cross Sections. We now examine the shape of the excitation function (cross section vs translational energy) with the associated 68% error bars for removal of $\text{O}_2(v)$ via reactive collisions (i.e., in processes leading to the formation of $\text{O}_3^*/\text{O}_3 + \text{OH}$, $\text{O}_2 + \text{O}_2 + \text{H}$, and $\text{O}_2 + \text{OH} + \text{O}$), which is shown in Figure 7. (Similar considerations apply to the excitation functions for $\text{O}_2(v)$ removal only via the formation of $\text{O}_3^*/\text{O}_3 + \text{OH}$. Because their shapes differ only quantitatively, we show only the total reactive $\text{O}_2(v)$ removal in Figure 7.) Clearly, for values of v larger than a given threshold $v_C = 18$, such curves have in general two opposite trends that explain their shapes. At low energies, the capture type regime dominates leading to the well-established^{68–70} decreasing dependence of σ^r with E_{tr} . For high translational energies, one observes instead the common pattern found in reactions that have an energy threshold; that is, σ^r is an increasing function of E_{tr} . As a result, the excitation function shows a minimum in the region where the two effects balance each other. It is interesting to note that σ^r increases slowly at high energies, suggesting that the capture type mechanism dominates over the whole range of translational energies. Such results lead to the conclusion that the high vibrational excitation in O_2 effectively promotes the rupture of the OO bond of the HO_2 radical while enhancing the role of long-range forces in the formation of $\text{O}_3^*/\text{O}_3 + \text{OH}$, $\text{O}_2 + \text{O}_2 + \text{H}$, and $\text{O}_2 + \text{OH} + \text{O}$. For $v < v_C$, chemical reaction occurs always with an activation energy, with reactivity increasing with translational energy.

To describe analytically the dependence of the cross section with translational energy, we have used the form

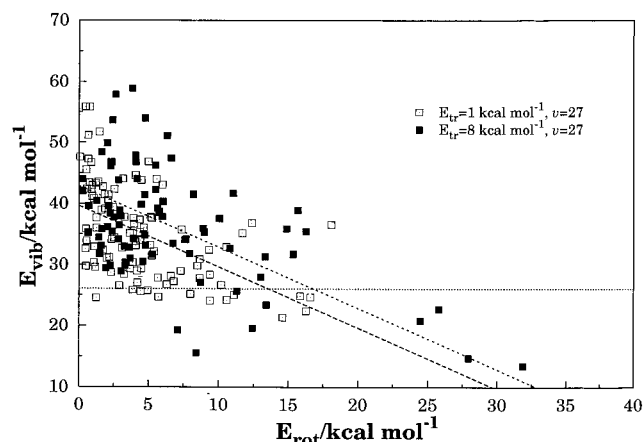
$$\sigma^x(E_{tr}, v) = \mathcal{A}(E_{tr}, v) + \mathcal{B}(E_{tr}, v) \quad (v \geq v_C, \forall E_{tr}) \quad (10)$$

$$= \mathcal{B}(E_{tr}, v) \quad (v < v_C, E_{tr} \geq E_{tr}^{\text{th}}) \quad (11)$$

$$= 0 \quad (v < v_C, E_{tr} < E_{tr}^{\text{th}}) \quad (12)$$

TABLE 4: Energies (in kcal mol⁻¹) and Percentages of Energy Partitioned to Different Degrees of Freedom for the Reaction O₂(*v*) + HO₂ → O₃^{*}/O₃ + OH

<i>v</i>	<i>E_{tr}</i>	$\langle E_{tr} \rangle$	$\langle E_{tr} \rangle$ (%)	O ₃ [*] /O ₃				OH			
				$\langle E_v \rangle$	$\langle E_v \rangle$ (%)	$\langle E_r \rangle$	$\langle E_r \rangle$ (%)	$\langle E_v \rangle$	$\langle E_v \rangle$ (%)	$\langle E_r \rangle$	$\langle E_r \rangle$ (%)
18	1.0	7.62	18.9	21.34	53.0	9.14	22.7	1.70	4.2	0.45	1.1
	2.0	8.13	19.6	29.34	70.7	0.97	2.3	1.05	2.5	2.00	4.8
	4.0	8.18	18.8	30.19	69.6	0.39	1.0	1.69	3.9	2.95	6.8
	6.0	10.31	22.7	26.90	59.2	3.34	7.3	2.58	5.7	2.32	5.1
	8.0	9.60	20.3	27.01	57.0	5.95	12.6	2.74	5.8	2.10	4.4
20	1.0	8.56	18.3	27.95	59.9	3.58	7.7	2.99	6.4	3.58	7.7
	2.0	11.70	24.5	27.51	57.7	3.85	8.1	2.24	4.7	2.36	5.0
	4.0	10.92	22.0	28.62	57.7	4.93	9.9	2.42	4.9	2.69	5.4
	6.0	13.55	26.0	28.36	54.4	4.01	7.7	3.00	5.8	3.18	6.1
	8.0	13.85	25.9	30.41	56.9	4.25	7.9	2.82	5.3	2.15	4.0
	12.0	14.01	24.4	33.63	58.5	4.18	7.3	2.47	4.3	3.19	5.5
	16.0	19.03	31.0	31.71	51.6	4.31	7.0	3.75	6.1	2.63	4.3
24	1.0	16.85	29.1	32.33	55.8	3.31	5.7	2.60	4.8	2.85	4.9
	2.0	15.72	26.7	32.66	55.4	4.29	7.3	3.72	6.3	2.56	4.3
	4.0	16.08	26.4	34.16	56.2	4.71	7.7	2.64	4.3	3.23	5.3
	6.0	18.35	29.2	34.12	54.3	4.54	7.3	2.50	4.0	3.30	5.3
	8.0	17.89	27.6	33.85	52.2	5.98	9.2	3.14	4.8	3.93	6.1
	12.0	21.22	30.9	34.76	50.6	6.54	9.5	2.86	4.2	3.31	4.8
27	1.0	18.94	28.9	35.14	53.7	4.51	6.9	3.01	4.7	3.89	5.9
	2.0	19.09	28.7	35.77	53.8	5.36	8.1	3.18	4.8	3.06	4.6
	4.0	21.39	31.3	35.18	51.5	5.08	7.4	3.25	4.8	3.44	5.0
	6.0	22.29	31.7	36.52	52.0	5.03	7.2	2.84	4.0	3.58	5.1
	8.0	22.64	31.3	36.27	50.2	6.60	9.1	3.00	4.2	3.72	5.2
	12.0	25.34	33.3	36.81	48.4	6.96	9.2	3.41	4.5	3.51	4.6

**Figure 5.** Vibrational-rotational energy distribution of products O₃^{*}/O₃. The dotted line indicates the threshold energy for dissociation into O₂ + O, while in dash are shown lines for the constant *E_{vib}* + *E_{rot}*.

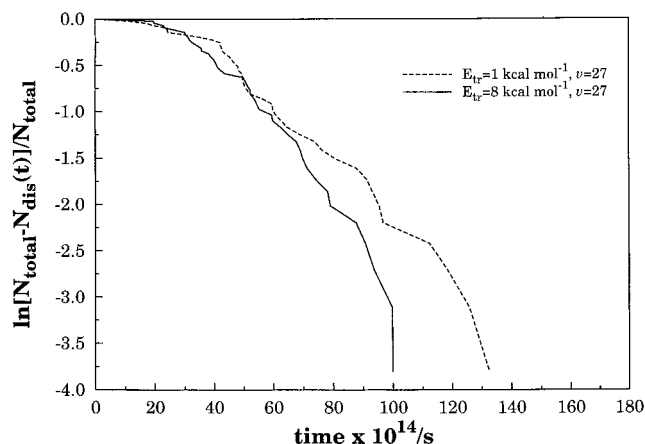
where the capture type contribution is defined by

$$\mathcal{C}(E_{tr}, v) = \frac{\sum_{i=1}^{n_C} c_i \Delta v^i}{E_{tr}^{n_1}} \quad (13)$$

and the barrier type term is written as

$$\mathcal{B}(E_{tr}, v) = [E_{tr} - E_{tr}^{\text{th}}(v)]^{n_2} \left(\sum_{j=0}^{n_B} d_j \Delta v^j \right) \exp[-m(E_{tr} - E_{tr}^{\text{th}}(v))] \quad (14)$$

Thus, *v_C* is the lowest value of *v* above which capture plays an important role. In turn, the *v*-dependent threshold energy has

**Figure 6.** Logarithm of the decay rate of O₃^{*} as a function time.

been found to be well-described by the form

$$E_{tr}^{\text{th}}(v) = A + b\Delta v \quad v < v_C \quad (15)$$

$$= 0 \quad v \geq v_C \quad (16)$$

where $\Delta v = v - v_{\text{th}}$ and v_{th} is the threshold vibrational quantum number above which reaction can in principle take place at zero translational energy. The above model excitation function provides therefore a generalization of that employed elsewhere,⁶² with the number of parameters and specific algebraic details being chosen to improve the quality of fit to the calculated data. From energetic requirements, we first fixed $v_{\text{th}} = 11$. Using this value and the calculated threshold energies, we have then determined that $v_C = 18$. In fact, eq 15 is found to fit accurately the calculated threshold energies, leading to a prediction of a zero threshold energy for $v_{\text{th}} = 18.6$, which has been rounded off to $v_C = 18$. We emphasize that the first term in eq 10 describes the *v*-dependent capture contribution of the cross section, while the second term represents the threshold energy type component. Except for $m = 0.05$, which has been kept for

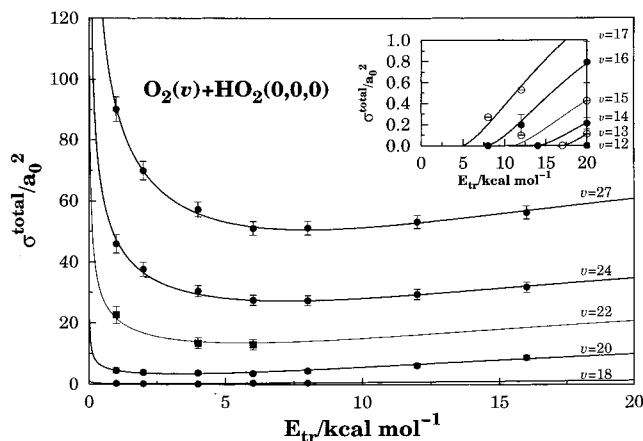


Figure 7. Reactive cross section σ^{total} as a function of the translational energy for products ($\text{O}_3^*/\text{O}_3 + \text{OH}$, $\text{O}_2 + \text{O}_2 + \text{H}$, and $\text{O}_2 + \text{OH} + \text{O}$). Shown in the insert are the cross sections for $v \leq 17$. The solid symbols correspond to the calculated cross sections while the open circles have been obtained by interpolation using the former. In all cases, the rotational quantum number of O_2 has been fixed at $j = 1$, while the rotational energy of HO_2 has been assigned by using the microcanonical sampling scheme for a temperature of 300 K. Also indicated when appropriate are the 68% error bars. The model in eq 10–16, calibrated using only the solid and open circles, is also shown by the thick and thin (predicted) solid lines.

TABLE 5: Numerical Values of Least-Squares Parameters in Eq 10–15^a

parameter	$v \geq v_C$	$v < v_C$
c_1	24.8566	nr ^b
c_2	-8.742 19	nr
c_3	1.045 40	nr
c_4	-4.906 94(-2) ^c	nr
c_5	8.246 67(-4)	nr
d_0	-9.217 32(-1)	8.125 42(-2)
d_1	2.740 08(-1)	-4.823 66(-2)
d_2	-2.888 41(-2)	1.118 11(-2)
d_3	1.428 11(-3)	-5.888 44(-4)
d_4	-2.408 23(-5)	-1.936 23(-5)
n_1	0.397 506	nr
n_2	1.863 13	1.50
m	0.05	0.05
A	nr	23.0713
b	nr	-3.041 66

^a Units are such that with the energy in kcal mol^{-1} , the cross section is in a_0^2 . ^b Not relevant. ^c Given in parentheses are the powers of 10 by which the numbers should be multiplied.

convenience from previous work,^{62,63} all other parameters have been determined from a least-squares fitting procedure to the calculated data. This fit consisted of two steps. First, we have fixed $n_C = 3$ and $n_B = 2$, with the model being calibrated from a fit to the calculated cross sections for $v \geq v_C$. Using this model with a reasonably small number of parameters, we then predicted the cross sections for $v = 35$ from a fit to the data for $v = 18, 20, 24,$ and 27 . These were then included as guiding data with half the weight of the calculated points to determine the least-squares parameters $n_1, c_i,$ and d_i in the final model with $n_C = 5$ and $n_B = 4$. Indeed, this model containing five additional parameters was judged to be the best overall, being the optimum values of the least-squares parameters reported in Table 5 (although the standard errors can be large for the smaller coefficients, we report for the sake of reproducibility all the numbers used in our calculations). The fit was completed by using now only eq 14 to fit the data for $v < v_C$. Given the scarcity of calculated points, we provide a coverage of such low vibrational states by interpolating linearly the cross section

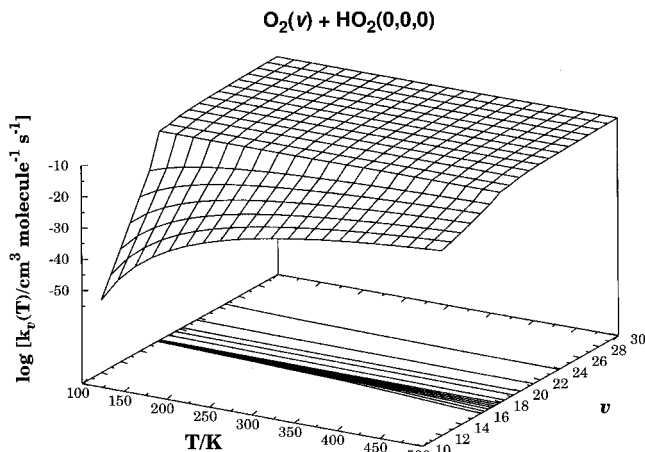


Figure 8. Total reactive thermal rate coefficient for $\text{O}_2(v) + \text{HO}_2$ as a function of temperature and vibrational quantum number of O_2 .

using the two closest calculated ones for a given translational energy, e.g., $v = 14$ and 16 in the case of $v = 15$. These new points are indicated using open symbols, while the new set of numerical coefficients (d_i) is also given in Table 5.

Figure 7 shows the calculated cross sections for the reactive removal of $\text{O}_2(v)$, together with the model excitation function in eq 10–16. Clearly, the fitted form shows very good agreement with the calculated points and hence highlights the trends involved. It also suggests that it may be reliable in predicting the cross section for other v states not specifically considered in this work, as it can be seen from the data calculated for $v = 22$ (using only 10^3 trajectories per point), which has not been included in the least-squares fitting procedure. Of course, care must be exercised when using the above model excitation function to extrapolate far beyond the range of v and E_{tr} values considered in the fit (shown by the solid dots and open circles in Figure 7).

By substitution of the above model excitation function in eq 4, the specific thermal rate coefficient assumes the general form

$$k_v(T) = g_e(T) \left(\frac{8}{\pi\mu} \right)^{1/2} \left\{ \left(\sum_{i=1}^{n_C} c_i \Delta v^i \right) \Gamma(2 - n_1) (RT)^{-n_1+1/2} + \left(\sum_{j=0}^{n_B} d_j \Delta v^j \right) \frac{(RT)^{n_2+1/2} \exp[-E_{\text{tr}}^{\text{th}}(v)/RT]}{(1 + mRT)^{n_2+2}} \times \left[\Gamma(n_2 + 2) + \Gamma(n_2 + 1) (1 + mRT) E_{\text{tr}}^{\text{th}}(v)/RT \right] \right\} \quad (17)$$

where $\Gamma(\dots)$ is the gamma function and all other symbols have their usual meaning. For $v \geq v_C$, one has $E_{\text{tr}}^{\text{th}} = 0$ while for $v < v_C$ one must use $c_i = 0$ ($i = 1 - n_C$) with the proper value of $E_{\text{tr}}^{\text{th}}$ and corresponding set of d_i coefficients (see Table 5). Following ref 62, we show in Figure 8 a perspective plot of the total reactive rate constant (i.e., for formation of products, $\text{O}_3^*/\text{O}_3 + \text{OH}$, $\text{O}_2 + \text{O}_2 + \text{H}$, and $\text{O}_2 + \text{OH} + \text{O}$) as a function of temperature and vibrational quantum number of O_2 . The notable feature is the significant variation in the temperature dependence pattern with vibrational quantum number. While for low vibrational states ($v \geq 12$) the rate constant increases with T as in a typical energy threshold regime, for high v states, such a dependence is less marked or even disappears stressing the dominant behavior of a capture type mechanism. Also observable is a somewhat sudden variation when going from $v = 17$ to 18 at a fixed temperature, which is due to the transition

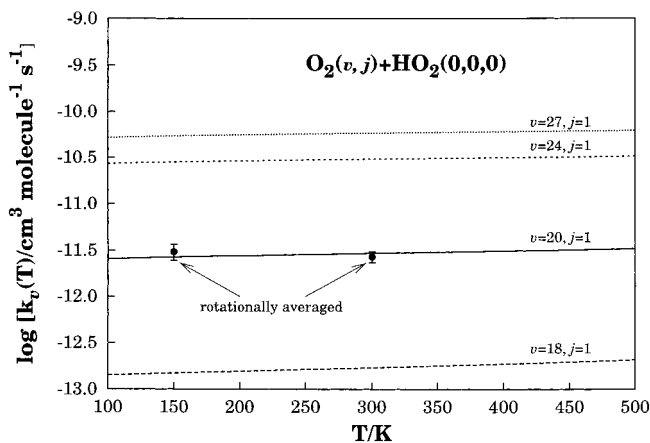


Figure 9. Cuts in Figure 8 for $v = 18, 20, 24,$ and 27 . The dots indicate the results of calculations using thermally averaged rotational distributions for O_2 .

TABLE 6: Calculated Specific Rate Coefficients for Formation of All Products at 298 K in $cm^3 s^{-1}$

v	$k(v)$
18	1.70(-13)
20	2.93(-12)
24	3.04(-11)
27	5.83(-11)

from a pure barrier type to a mixed mechanism where capture also takes place. For completeness, Table 6 compares the calculated thermally averaged specific rate coefficients at 298 K. In turn, Figure 9 shows cuts of Figure 8 for $v = 18, 20, 24,$ and 27 . Clearly, the rate constants are seen to vary by almost 3 orders of magnitude when going from $v = 18$ to 27 , being quite large for high v states. Also shown by the dots in Figure 9 are the results obtained from rotationally averaged calculations for $v = 20$ using 2×10^3 trajectories. They suggest that the trends reported in this work for O_2 kept at $j = 1$ should not differ drastically from those obtained for a thermalized rotational distribution.

5. Conclusions

We reported a theoretical study of the title multichannel reaction, which to our knowledge, provides the first information on collisions of vibrationally excited molecular oxygen with hydroperoxyl radicals. It has been shown that the product ozone molecules are formed with a substantial amount of internal energy, both vibrational and rotational. Such molecules lead ultimately to the formation of stable ozone species via either a quenching mechanism or through dissociation followed by fast recombination of the formed oxygen atom in excess of molecular oxygen. The calculations also suggest that for $v \geq 18$, reaction occurs via both capture type and barrier type mechanisms for low and high translational energies, although reactive $O_2(v)$ removal via a capture type mechanism seems to dominate over the whole range of translational energies. No comparison with experimental data has been possible due to the unavailability of such data. We hope that the present study may stimulate work using laser techniques that allow the preparation of vibrationally hot reactant molecules.

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