A quasiclassical trajectory study of the OH plus SO reaction: The role of rotational energy

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A quasiclassical trajectory study of the \( \text{OH} + \text{SO} \) reaction: The role of rotational energy

M. Y. Ballester, Y. Orozco-Gonzalez, J. D. Garrido, and H. F. Dos Santos

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A full dimensional quasiclassical trajectory study of the \( \text{OH} + \text{SO} \) reaction is presented with the aim of investigating the role of the reactants rotational energy in the reactivity. Different energetic combinations with one and both reactants rotationally excited are studied. A passive method is used to correct zero-point-energy leakage in the classical calculations. The reactive cross sections, for each combination, are calculated and fitted to a capturelike model combined with a factor accounting for recrossing effects. Reactivity decreases as rotational energy is increased in any of both reactants. This fact provides a theoretical support for the experimental dependence of the rate constant on temperature. © 2010 American Institute of Physics. [doi:10.1063/1.3303202]

I. INTRODUCTION

The SO radical plays a significant role in combustion chemistry\(^1\) while atmospheric oxidation of sulfur is believed to be driven by hydroperoxyl radicals.\(^2\) The reaction

\[
\text{OH} + \text{SO} \rightarrow \text{H} + \text{SO}_2
\]  

(1)

has been extensively studied, both theoretically\(^3\)–\(^7\) and experimentally.\(^8\)–\(^10\) In a previous work\(^11\) a quasiclassical trajectory study of reaction 1 was reported, providing details on reaction mechanism and reactive rate constant. In the previous theoretical works the initial rovibrational states of the reactants were fixed at their corresponding ground level.

Several works have reported the influence of OH rotational energy in reactions with atoms. In a work by Jorfi et al.\(^12\) an enhancement of rate constant, as rotational energy is initially deposited in the hydroxyl radical for the reaction \( \text{OH} + \text{O} \rightarrow \text{H} + \text{O}_2 \), was obtained. Large effects in reactive cross section and rate constant were observed for N+OH collision\(^13\) when rotational quantum number of OH \( (j_{\text{OH}}) \) is increased. However, almost no change was observed in reactivity when OH rotational energy is raised in C+OH collision.\(^14\) A quantum dynamics study of the title reaction was presented by Clary\(^15\) using models of adiabatic capture with a dipole-dipole potential type. In that study\(^15\) a quantum model to describe reaction 1 was developed; improvements are now timely and relevant. We shall comment further on this work in Sec. IV.

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

\[
\text{OH}(v' = 0, j_{\text{OH}}) + \text{SO}(v'' = 0, j_{\text{SO}}) \rightarrow \text{H} + \text{SO}_2,
\]  

(2)

by using the quasiclassical trajectory method\(^16\) and a previously reported single-valued potential energy surface (PES) for the ground electronic state of HSO\(_2\).\(^17\) aiming to investigate the effects of reactant’s rotational energy. The paper is organized as follows: the next section gives a brief description of the properties of the PES, while the calculation methodology is presented in Sec. III. The results are discussed in Sec. IV and the main conclusions are given in the last section.

II. PES

All calculations reported in this work have employed the six-dimensional double many-body expansion (DMBE) PES for the ground electronic state of HSO\(_2\).\(^17\) It employs realistic DMBE functions previously reported for the diatomic and triatomic fragments (see Ref. 17 and references therein) and four-body energy terms to mimic \textit{ab initio} CASPT2/FVCAS/AVXZ \((X=D,T)\) calculations for the tetrameric system. Since such a potential function has already been described in detail elsewhere,\(^17\) we focus on features which are of relevance for the title reaction.

Figure 1 presents a contour plot for reaction 1, according to HSO\(_2\) DMBE PES. The same nomenclature used before\(^15\) is applied here. Thus, HOSO stands for the global minimum with the hydrogen atom bonded to the oxygen, lying 71.8 kcal mol\(^{-1}\) below OH+SO limit. Note the absence of a barrier for the reactants to produce intermediate species. For the energy range studied in this work no other products are energetically allowed to be formed.

A salient feature of the DMBE PES of interest in the present work is the predicted reaction enthalpy. Using the zero point energy values on DMBE PES and the calculated partition functions one gets \( \Delta H^o_0 = -30.2 \text{ kcal mol}^{-1} \) and \( \Delta H^0_{298.15} = -31.8 \text{ kcal mol}^{-1} \). In a recent work,\(^18\) Wheeler and

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Schaefer III presented an ab initio study on HOSO radical. Combining the enthalpy values there reported produce $\Delta H^0 = -29.4$ kcal mol$^{-1}$ for reaction 1. This latter value is very close to the one predicted by the DMBE PES at 0 K.

The HSO$_2$ DMBE PES was used in a quasiclassical trajectory study of the reaction

$$\text{H} + \text{SO} \rightarrow \text{OH} + \text{SO}. \quad (3)$$

Rate constant values there obtained are in very good agreement with the experimental data. These above-mentioned issues make the DMBE PES accurate and reliable for describing interaction of HSO$_2$ molecular system, as required for this work.

III. COMPUTATIONAL PROCEDURES

For obtaining the quasiclassical trajectories we have utilized an adapted version of the VENUS96 (Ref. 20) code which accommodates the HSO$_2$ DMBE PES. Such a methodology has been used to assess the role of vibrational excitation of the reactants in processes such as HS+O$_2$. The quasiclassical trajectories (QCT) has also been employed to study the effects of OH rotational energy in molecular collisions, particularly in (C, O, N)+OH reactions. 12-14

As before each trajectory may lead to 14 distinguishable channels without considering the various possible triatomic isomers. Nevertheless only channel 1 is energetically allowed to be opened, for the range of internal and translational energies studied in this work.

As we are looking for the influence of the rotational energy in the reactivity of the title reaction, we have used in QCT calculations initial rotational quantum numbers in the range: $1 \leq j_{OH} \leq 12$ for the OH radical and we have selected values that are multiples of five in the range: $0 \leq j_{SO} \leq 60$ for SO. Additional QCT calculations were carried out with both reactants rotationally excited for comparison with experimental data. Vibrational quantum numbers of both reactants have been fixed at the ground levels $v' = 0$ and $v'' = 0$ for all calculations. To model the dependence of rotational energy with the rotational quantum numbers $j_{OH}$ and $j_{SO}$ we have assumed the rigid rotor approximation, considering the relative small values of the used quantum numbers and that the molecule is at the ground vibrational level. The ground electronic state of OH belongs to Hund’s case (a) or (b) or a mixture of them. In this work we assume the case (b), once for a fast rotating OH this case is expected to dominate. Hence the rotational quantum number is given by $j_{OH} = 1, 2, \ldots$, with the smallest value being $j_{OH} = 1$. $\Lambda$ is the associated electronic angular momentum.

The determination of the step size for numerical integration has been made by trial and error on the basis of accuracy requirements. A value of $2.5 \times 10^{-16}$ s for the step size for numerical integration has been found sufficient to warrant conservation of total energy to better than one part in $10^3$. Reactant molecules were initially separated by 10 Å, a value considered sufficiently large to make the interaction energy essentially negligible. To select the maximum value of the impact parameter ($b_{max}$) which leads to reaction, we have followed the usual procedure by computing batches of 100 trajectories for fixed values of $b$. This procedure should allows an accuracy in $b_{max}$ of about ±0.1 Å. Batches of 2000 trajectories were calculated for each translational and rotational energy combination. Such a number of trajectories has been found to be enough to yield reactive cross sections with an error of typically a few percent.

For a given set of initial translational ($E_{tr}$) and rotational energy of the reactants (defined by rotational quantum numbers $j_{OH}$ and $j_{SO}$), the reactive cross section is given by

$$\sigma_R(E_{tr}; j_{OH}; j_{SO}) = \frac{\pi b_{max}^2}{E_{tr}} \left( \frac{E_{tr}}{k_B T} \right)^{1/2},$$

and the associated uncertainty is

$$\Delta \sigma = \left( \frac{N_T - N_i}{N_T N_i} \right)^{1/2} \sigma_R,$$

where $N_i$ is the number of reactive trajectories in a total of $N_T$ and $P_r = N_r/N_T$ is the reaction probability. Assuming a Maxwell–Boltzmann distribution over the translational energy, the specific thermal rate coefficient is obtained as

$$k(T; j_{OH}; j_{SO}) = g_e(T) \left( \frac{2}{k_B T} \right)^{3/2} \left( \frac{1}{\pi \mu} \right)^{1/2} \times \int_0^\infty E_u \sigma_R(E_u; j_{OH}; j_{SO}) \exp \left( - \frac{E_u}{k_B T} \right) dE_u,$$

where $T$ is the temperature, $\mu$ is the reactants reduced mass, $k_B$ is the Boltzmann constant, and $g_e(T)$ the electronic degeneracy factor, which assumes the form

$$g_e(T) = \frac{1}{3 \left[ 1 + \exp(-205/T) \right]}.$$

To monitor complex formation we have first studied batches of 100 trajectories for selected combinations of initial rotation quantum numbers and collision energy. By the examination of bond-distances and potential energy versus time plots, we found that when atoms get closer (all the interatomic distances shorter than 3.5 Å) the potential energy falls to
values below the H+SO \textsubscript{2} limit. Thus, according to the DMBE PES, \textsuperscript{17} only configurations of an excited HOSO or an excited HSO\textsubscript{2}, a local minimum in a C\textsubscript{s} configuration, are allowed to be formed. Furthermore, in such plots was verified that the HS bond-distance remains larger than both of the OH ones. Then, the formed intermediate structure corresponds to an HOSO configuration. To implement complex formation in the code, we defined the complex as any structure where the HS and SO\textsubscript{a} is the oxygen in the incoming OH) become shorter than 1.3 times their corresponding values at the global minimum. Such a definition leads to complex lifetimes that agree well with those obtained from direct calculations. Some trajectories forming HOSO complex remain ambiguity and we use here a simple “nonactive” method, vibrational quantum mechanical threshold method (VEQMT\textsubscript{C}), \textsuperscript{28} and assume that the number of trajectories is large enough as to change little the original sampling. Following this method, only those trajectories for which the total vibrational energy of the products exceeds the sum of their corresponding ZPEs are included in the statistical analysis.

### IV. RESULTS AND DISCUSSION

Table I collects results for trajectory calculations when one of the reactants is rotationally excited and both reactants are rotationally excited. For brevity only three combination of the rotational quantum numbers were included.\textsuperscript{29} There, \(N_{\text{com}}\) is the number of trajectories forming a complex, while \(N_{\text{rec}}\) is the number of recrossing trajectories, i.e., those trajectories which break down the complex into reactants. For the internal and translational energies considered in the present work it is verified (see Table I) that \(N_{\text{com}}=N_{\text{rec}}+N_{r}\). Thus, all reactive trajectories produce first an HOSO adduct. Average complex lifetime depends upon both translational and rotational energies of the reactants. Longer lifetimes were observed for the lower combinations of initial rotation quantum numbers and collision energy, favoring then randomization of the energy and hence products formation. For combinations with a higher content of internal and translational energies, short lifetimes were observed producing lower reactivities.

The OH+ SO reaction is dominated by long range multipolar forces. Reactants are captured by a deep well forming HOSO. This issue is relevant in the convergence of the calculations. Some trajectories forming HOSO complex remain

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oscillating around such a configuration for large number of iteration steps. This situation increases the computational cost of the calculation and produces very few (less than 2%) nonconvergent trajectories.

In Table I QCT values are compared with those obtained by the VEQMTC method. Notice that much of the difference between both methods comes from the large number of re-crossing trajectories \( N_{\text{rec}} \) not fulfilling the requirements of VEQMTC. The above-mentioned effect diminishes when the reactivity trend is only to be taken into account. From inspection of Fig. 2 it becomes apparent that the reactivity decreases as the rotational energy is increased. Thus part of the rotational energy is converted into vibrational energy of the molecules in nonreactive trajectories. As before, for lower and upper limits of reactivity we used QCT and VEQMTC, respectively.

In Fig. 2, the standard QCT excitation functions for low translational energies are presented. Some rotational combinations were included there. Excitation functions show a common pattern typically observed in capturelike reactions. From inspection of Fig. 2 it becomes apparent that the reactivity decreases as the rotational energy increases. Such assertion can be better illustrated by means of the plot of reactive cross sections versus \( j_{\text{OH}} \) presented in Fig. 3. There, the reactive cross sections were normalized to the corresponding values for the ground rotational level \( j_{\text{OH}}=1, j_{\text{SO}}=0 \). Only low translational energies versus \( j_{\text{OH}} \) were there represented. Larger translational energies will be discussed later in this section. Comparing the plot in Fig. 3 with those reported for \( \text{D}+\text{H}_2 \) reaction, we find a similar behavior; there is a decrease in the reactive cross section as rotational quantum number is raised.

The analysis in the previous paragraph is based on results with only one rotationally excited reactant and for translational energies below 2.0 kcal mol\(^{-1}\). Panels in Fig. 4 display normalized QCT cross sections versus total rotational energy of the reactants. Trend lines were also included in these plots. There, no difference was observed when rotational energy was deposited either in OH or in SO. Instead, a single dependence of the reactivity on the total rotational energy is obtained. Another significant conclusion from these plots is that increasing the rotational energy largely affects the reactivity for low translational energies, while for large translational energies there is almost no effect in reactivity as rotational energy is increased in the reactants. This behavior is probably produced by the changes in long range interactions due to rotation, more relevant at low translational energies since the molecules have then time to reorient during the course of collision.

Being a barrierless process, the reactive cross section can be expressed by

\[
\sigma(E_{tr};E_{th}) = n \pi(n-2)^{(2-n)/n} \times \left( \frac{C_n}{2E_{tr}} \right)^{2/n} F_{\text{rec}}(E_{tr};E_{th}),
\]

where the first term represents the capture cross section and \( F_{\text{rec}}(E_{tr};E_{th}) \) accounts for re-crossing effects. The dependence of reactive cross section on reactants rotation is represented by the parameter \( E_{th} \) denoting the total rotational excitation energy of the reactants. The recrossing factor \( F_{\text{rec}} \) reported in a previous paper depends on a threshold energy value \( E_{th}^{\text{th}} \) as

\[
F_{\text{rec}}(E_{tr}) = \begin{cases} 
1 & E_{tr} < E_{th}^{\text{th}} \\
\exp[- \alpha(E_{tr} - E_{th}^{\text{th}})] & E_{tr} \geq E_{th}^{\text{th}}
\end{cases}
\]

In this work we found that when reactants appear in excited rotational levels such threshold energy vanish. Thus, a different model than the previously used is here proposed

\[
F_{\text{rec}} = \exp[- \alpha(E_{tr} + E_0)].
\]

This expression denotes that the probability for the reaction to take place once the complex is formed is inversely proportional to certain effective value of the energy. This is given by the sum of the initial translational energy and an amount of energy depending on the internal energy of the reactants \( E_{tr} + E_0 \); in other words, the probability of a trajec-
tory to recross back to reactants after forming a complex ($P_{rec} = N_{rec}/N_{com}$) is increased when such effective energy is raised. Thus, the value of $E_0$ is expected to be related to the initial energy content in reactants. Furthermore, in the case of VEQMTC analysis $E_0$ must be lower than for pure QCT. Both previous statements were verified when fitting $1 - P_{rec}$ to Eq. (10) via $\alpha$ and $E_0$. Table II collects the coefficients for such a fitting, for QCT and VEQMTC. Also presented in Table II are the $n$ and $C_n$ values from fitting reactive cross section to Eq. (8). Note that $n$ gets values between the corresponding ones for interactions dominated by dipole-dipole ($n=3$) and dipole-quadrupole ($n=4$).

After substitution of Eq. (8) in Eq. (6) and integration, one gets

$$k(T) = k_{cap}(T) \frac{\exp(-\alpha E_0)}{\left(1 + \frac{T}{T_0}\right)^{2(n-1)/n}},$$

(11)

then, the rotationally averaged rate constant is

$$k_{cap}(T) = 2n \pi \gamma e(T) (n-2)/(2-n)/n \times \left(\frac{2}{\pi \mu}\right)^{1/2} (k_B T)^{(n-4)/2n} \times \left(\frac{C_n}{2}\right)^{2/n} \Gamma\left[\frac{2(n-1)}{n}\right],$$

(12)

where $T_0 = 1/(\alpha k_B)$.

To judge the role of the rotational excitation of reactants in the reactivity of the OH+SO collisional process, we employ an average rate constant. For this, we used a population distribution, depending on temperature as

$$P_j(T) = A(2j + 1) \exp\left(\frac{-B j (j + 1)}{k_B T}\right),$$

(13)

where $A$ is a normalization constant, warranting

$$\sum_{j=1}^{k} P_j(T) = 1,$$

(14)

Then, the total rotational excitation energy of the reactants is presented in the second column.

<table>
<thead>
<tr>
<th>$j_{OH}$, $j_{SO}$</th>
<th>$E_{int}^{b}$</th>
<th>$n$</th>
<th>$C_n$</th>
<th>$\alpha$</th>
<th>$E_0^{b}$</th>
<th>$n$</th>
<th>$C_n$</th>
<th>$\alpha$</th>
<th>$E_0^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 0</td>
<td>0.000</td>
<td>3.9102</td>
<td>202.73</td>
<td>0.10</td>
<td>4.84</td>
<td>3.9763</td>
<td>213.79</td>
<td>0.09</td>
<td>0.86</td>
</tr>
<tr>
<td>1, 5</td>
<td>0.061</td>
<td>3.9499</td>
<td>205.40</td>
<td>0.08</td>
<td>6.43</td>
<td>3.9143</td>
<td>186.06</td>
<td>0.08</td>
<td>1.28</td>
</tr>
<tr>
<td>1,10</td>
<td>0.226</td>
<td>3.5667</td>
<td>113.85</td>
<td>0.10</td>
<td>4.81</td>
<td>3.9133</td>
<td>174.08</td>
<td>0.11</td>
<td>0.46</td>
</tr>
<tr>
<td>3, 0</td>
<td>0.529</td>
<td>3.9877</td>
<td>204.24</td>
<td>0.08</td>
<td>6.97</td>
<td>3.9482</td>
<td>160.81</td>
<td>0.11</td>
<td>0.69</td>
</tr>
<tr>
<td>3,10</td>
<td>0.754</td>
<td>3.7349</td>
<td>129.55</td>
<td>0.13</td>
<td>3.77</td>
<td>3.7683</td>
<td>119.18</td>
<td>0.12</td>
<td>0.61</td>
</tr>
<tr>
<td>1,30</td>
<td>1.905</td>
<td>3.9676</td>
<td>146.97</td>
<td>0.11</td>
<td>5.61</td>
<td>3.8916</td>
<td>121.49</td>
<td>0.11</td>
<td>1.49</td>
</tr>
<tr>
<td>6, 0</td>
<td>2.109</td>
<td>3.9756</td>
<td>150.38</td>
<td>0.08</td>
<td>8.00</td>
<td>3.9950</td>
<td>122.43</td>
<td>0.10</td>
<td>1.98</td>
</tr>
<tr>
<td>5,20</td>
<td>2.339</td>
<td>3.7646</td>
<td>100.20</td>
<td>0.10</td>
<td>6.04</td>
<td>3.8013</td>
<td>86.30</td>
<td>0.11</td>
<td>1.51</td>
</tr>
<tr>
<td>10, 0</td>
<td>5.655</td>
<td>3.9583</td>
<td>118.65</td>
<td>0.06</td>
<td>14.45</td>
<td>3.9543</td>
<td>97.66</td>
<td>0.10</td>
<td>4.66</td>
</tr>
<tr>
<td>8,35</td>
<td>6.259</td>
<td>3.7559</td>
<td>56.94</td>
<td>0.09</td>
<td>9.16</td>
<td>3.7140</td>
<td>44.47</td>
<td>0.10</td>
<td>4.66</td>
</tr>
</tbody>
</table>

Units are such that $\alpha$ in Eq. (8) is expressed in Å$^2$ when $E_0$ is in kcal mol$^{-1}$.

In kcal mol$^{-1}$.

FIG. 4. Normalized cross section versus total rotational excitation energy of the reactants ($E_{int}^{OH} + E_{int}^{SO}$). Panels on top stand for low translational energies and bottom panels represent high translational energies studied in this work. Solid lines represent the trend of each set of points.
FIG. 5. Rate constant for the title reaction. Experimental data with the corresponding error bars are represented. Shaded region stands for rotationally averaged results obtained in this work; QCT and VEQMTC produces lower an upper limits, respectively.

\[
\langle k \rangle = \sum_{J_{OH}=1}^{12} \sum_{J_{SO}=0}^{60} P_{J_{OH}} P_{J_{SO}}(T) k(T; J_{OH}/J_{SO}).
\]

Instead of calculating all the rotational combinations in the previous equation, we used the idea that coefficients in Table II depends on \(E_{rot}\), no matter how such energy is distributed among reactants. Thus, each set of coefficients was fitted to linear functions on \(E_{rot}\). Then, we have

\[
k(T; J_{OH}/J_{SO}) = k(T; E_{rot}(J_{OH}/J_{SO})).
\]

Now compare this average rate constant with the literature. In a study of molecular collisions dominated by long-range forces, Clary\(^{15}\) pointed out that a negative dependence of the rate constant for reaction 1 is related to rotational effects. However, Blitz et al.\(^{10}\) rationalized their reported nonlinear decreasing of rate coefficient with temperature on the basis of the formation of the two adducts HOSO and HSO\(_2\) as intermediates for the reaction. Such analysis was supported by \textit{ab initio} studies\(^{5}\) concluding that isomerization HOSO \(\rightarrow\) HSO\(_2\) takes place in the pathway to the products (H + SO\(_2\)). As it was reported in a previous work\(^{11}\) and it is confirmed here, no formation of HSO\(_2\) has been observed during our quasiclassical studies. Direct dissociation from HOSO to products is observed instead.

Figure 5 displays the average rate constant versus temperature with the dark-filled region. As discussed in preceding paragraphs, upper limit stands for VEQMTC results while QCT provides the lower one. Experimental data available in the literature are also shown. Accounting for rotational energy of the reactants produces a negative dependence on temperature, more remarkable than for \(J_{OH}=1\), \(J_{SO}=0\).\(^{11}\) However, there is no concordance with the drastic falling for temperatures above 500 K reported by Blitz et al.\(^{10}\) Notice that below such a temperature our result agrees reasonably well with experimental data. For completeness we collect in Table III experimental rate constants and two theoretical values for the title reaction. The latter corresponds to quasiclassical calculations of this work with

<table>
<thead>
<tr>
<th>T/K</th>
<th>(k(J_{OH}=1))</th>
<th>(k(J_{OH}))</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>8.9–13.7</td>
<td>8.3–12.7</td>
<td>7.91 ± 1.58</td>
</tr>
<tr>
<td>298</td>
<td>8.9–13.6</td>
<td>8.3–12.6</td>
<td>11.6 ± 5.0(^a)</td>
</tr>
<tr>
<td>300</td>
<td>8.9–13.6</td>
<td>8.3–12.6</td>
<td>8.4 ± 1.5 (^b)</td>
</tr>
<tr>
<td>353</td>
<td>8.4–12.9</td>
<td>7.8–11.7</td>
<td>7.00 ± 1.40</td>
</tr>
<tr>
<td>403</td>
<td>8.1–12.3</td>
<td>7.4–11.1</td>
<td>5.53 ± 1.10</td>
</tr>
<tr>
<td>453</td>
<td>7.8–11.9</td>
<td>7.0–10.5</td>
<td>5.53 ± 1.10</td>
</tr>
<tr>
<td>503</td>
<td>7.5–11.5</td>
<td>6.7–10.1</td>
<td>5.11 ± 1.02</td>
</tr>
<tr>
<td>553</td>
<td>7.3–11.2</td>
<td>6.4–9.6</td>
<td>4.45 ± 0.89</td>
</tr>
<tr>
<td>603</td>
<td>7.1–10.9</td>
<td>6.2–9.2</td>
<td>3.66 ± 0.73</td>
</tr>
<tr>
<td>653</td>
<td>7.0–10.6</td>
<td>5.9–8.8</td>
<td>2.18 ± 0.43</td>
</tr>
<tr>
<td>703</td>
<td>6.8–10.3</td>
<td>5.8–8.5</td>
<td>1.44 ± 0.30</td>
</tr>
</tbody>
</table>

\(^a\)From Ref. 8.
\(^b\)From Ref. 9.

\(J_{OH}=1\), \(J_{SO}=0\) and the averaged ones. For such values, upper limits came from VEQMTC results while pure QCT stands for the lower limits.

As was shown in Fig. 4, for larger translational energies no significant effect in reactivity was observed as a result of increasing rotational energy of the reactants; while reactivity gets lower values as rotational energy is raised for low translational energies. Of course, for the range of temperatures we are reporting rate constant in this work, such a low translational energy region is the most significant.

V. CONCLUSIONS

The quasiclassical trajectory method have been used to study OH+SO collision. The reaction is dominated by long range forces and a capturelike behavior jointly with recrossing effects is observed. Selected rotational excited levels for the OH and the SO were studied. When rotational energy is deposited either in the OH or in the SO reactant, a decrease in reactivity is obtained. The reactive cross section depends upon the total rotational excitation energy deposited in both reactants together and the translational energy. The effects of rotation becomes more important for relatively low translational energies. The average rate constant reported here agrees reasonably well with experimental data below 500 K, while rotational effects are shown to be responsible for some of the negative dependence of the reaction rate constant on temperature.

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34. See supplementary material at 10.1063/1.3303202 for more data on trajectory calculations, fitted coefficients, and $\sigma_\theta$ versus $j_{SO}$ plot.  