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An accurate study of the dynamics of the C+OH reaction on the second excited $1^4A''$ potential energy surface

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The dynamics of the $C(3P)+OH(X^2\Pi) \rightarrow CO(a^3\Pi)+H(3S)$ on its second excited potential energy surface, $1^4A''$, have been investigated in detail by means of an accurate quantum mechanical (QM) time-dependent wave packet (TDWP) approach. Reaction probabilities for values of the total angular momentum $J$ up to $50$ are calculated and integral cross sections for a collision energy range which extends up to $0.1\ eV$ are shown. The comparison with quasi-classical trajectory (QCT) and statistical methods reveals the important role played by the double well structure existing in the potential energy surface. The TDWP differential cross sections exhibit a forward-backward symmetry which could be interpreted as indicative of a complex-forming mechanism governing the dynamics of the process. The QM statistical method employed in this study, however, is not capable to reproduce the main features of the possible insertion nature in the reactive collision. The ability to stop individual trajectories selectively at specific locations inside the potential energy surface makes the QCT version of the statistical approach a better option to understand the overall dynamics of the process.

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I. INTRODUCTION

The astrophysical interest of reactions between free radicals has motivated an ample list of recent studies of collisions between open-shell atoms such as $C(3P)$, $N(4S)$, $F(2p)$, $O(3P)$, or $S(3P)$ (Refs. 19 and 20) with the hydroxyl radical $OH(\Sigma^+\Pi)$. Practical difficulties to produce and measure radical concentrations made experimentalists to focus mainly on reactions which involve stable molecules. The development of new methods to investigate ultra low temperature kinetics, as the CRESU technique, revealed however that reactions between neutral species could govern the dynamics at low-temperature regimes, for instance, in interstellar clouds. Recent examples of the possibilities of such approaches have been reported for the $N+OH$ reaction. In those works, quasi-classical trajectory (QCT) and quantum mechanical (QM) calculations were performed to obtain reaction probabilities, cross sections, and rate constants. A comparison with measured rate constants was also presented in Ref. 10.

From a theoretical point of view, investigations have tackled not only the calculation of rate constants but the understanding of the precise dynamics of these collisions. The presence of open-shell species in both reactants and products adds an extra interest to study reactions of this sort. The existing electronic states may cross several times along the corresponding minimum energy path thus giving rise to avoided crossings and conical intersections. The corresponding multidimensional potential energy surfaces (PESs) exhibit a complex topology which usually involves several barriers and wells. The reaction mechanisms are then the result of the competition between direct and sequential pathways such as abstraction and complex-forming processes. Thus, the relatively simple landscape of possible dynamics typically attributed to triatomic systems may become as complex as those for polyatomic systems. The study of atom-diatom collisions constitute then ideal benchmarks to investigate the reaction dynamics by means of exact methods and to test approximate approaches to be employed in the description of more complicated mechanisms.

In line with this interest for the dynamical aspects of the above-mentioned processes, reaction probabilities and cross sections for $C(3P)+OH(X^2\Pi) \rightarrow CO+H(3S)$ have been analyzed to provide some insight about the mechanisms which rule these processes. A series of studies led to obtain the PESs corresponding to the states involved in the collision of the C atom with $OH(X^2\Pi)$ to produce $CO(X^3\Sigma^+)$ (the $X^2A'$ ground state) or $CO(a^3\Pi)$ (the first, $1^2A''$, and second, $1^4A''$, excited states) (Ref. 2).

The $C(3P)+OH(X^2\Pi) \rightarrow CO(X^3\Sigma)+H(3S)$ reaction on its ground electronic state is characterized by a large exothermicity ($-6.5\ eV$) and the absence of any barrier in the entrance channel. These features make accurate QM calculations very expensive in computational terms. Apart from QCT studies, the reaction on the $X^2A'$ state has been studied for nonzero values of the total angular momentum, $J$, and...
by means of a capture model combined with wave packet (WP) calculations.\(^5\) \((J > 0)\)-reaction probabilities, integral cross sections (ICSs), and rate constants were thus reported and compared with their QCT counterparts. Alternatively and in spite of some previous indications regarding the apparent preference for a direct reaction mechanism,\(^4\) statistically based approaches have also been employed to estimate QM ICSs and rate constants.\(^6\) Authors considered that the reason for the success of the capture approach implicit in the statistical model is that the nonreactive flux back to the reactants arrangement is essentially zero.

The analytical global PESs for the two electronically excited states were built by means of the reproducing kernel Hilbert space method, with the multi-reference internally contracted single and double configuration interaction level plus Davidson correction for the corresponding \textit{ab initio} calculations. The potential energy profiles for both \(^2A''\) and \(^2A'\) states of the \(\text{C}(^3P) + \text{OH}(^2\Pi) \rightarrow \text{CO}(^2\Pi) + \text{H}(^2S)\) reaction exhibit a double well structure with minima for the COH and HCO species and a noticeably smaller exothermicity \((-0.41\; eV)\) than in the case of the ground state. The depth of the corresponding wells on the first excited state, \(^2A''\), are \(-4.6\; eV\) for the COH minimum and \(-6.2\; eV\) for HCO, respectively. For the second excited state, \(^1A'\), those wells are less deep \((-1.85\; eV\) for COH and \(-2.25\; eV\) for HCO) and the surface exhibits five saddle points: Besides the two inversion barriers for the COH and HCO species (I1 and I2, respectively), there is one saddle point (SP1) in the HCO/COH isomerization barrier at \(-0.33\; eV\) relative to the entrance channel, and there are two more (SP2 and SP3) which correspond to the H–CO and CO–H dissociations with energies of \(-0.11\; eV\) and \(0.03\; eV\), respectively, measured from C+OH. A scheme with these stationary points of the surface is shown in Fig. 1. These features suggest that the reaction on the \(^1A'\) electronic state proceeds preferentially through the global minimum HCO.\(^2,19\)

Up to date, the only calculations performed on the second excited PES of the title reaction are those reported by Zanchet \textit{et al.}\(^2\) in which QCT calculations were performed to estimate the rate constant in combination with the other two reactive surfaces \(^2A''\) and \(^2A'\), and the study by means of a time-independent QM (TIQM) method by Jorfi and Honvault.\(^7\) In this last work, \(J = 0\) state-to-state reaction probabilities were calculated for the 0–0.9 \(eV\) collision energy, \(E_c\), range. A \(J\)-shifting approach was employed to calculate rate constants between 0 and 500 \(K\). Profound quantitative differences with respect to QCT results were found for a temperature above 50 \(K\).

In this paper we present for the first time accurate QM results for the \(\text{C} + \text{OH}(v = 0, \; j = 0) \rightarrow \text{CO}(\sigma^2\Pi) + \text{H}\) reaction on the \(^1A'\) PES. Reaction probabilities, ICSs and differential cross sections (DCSs) have been calculated by means of a time-dependent WP (TDWP) method. In addition QCT and statistical calculations have been performed in order to investigate the dynamics of the reaction. Their comparison with the TDWP give us some interesting details regarding the precise mechanisms which govern the process.

This paper is structured as follows: In Sec. II we describe the theoretical methods employed in the calculations; results are presented in Sec. III and discussed in Sec. IV. Finally, conclusions are shown in Sec. V.

II. METHODOLOGY

A. Time-dependent wave packet method

All TDWP calculations have been performed using the DIFFREALWAVE\(^{23,24}\) code. The parameters employed in the calculations are given in Table I. All calculations were carried out for the ground state of the reactants, \(\text{OH}(v = 0, \; j = 0, \; \Omega = 0)\). Results have been obtained for a range of collision energies between 0 \(eV\) and 0.45 \(eV\). Calculations for \(J = 0\)–50 have been carried out which included all Coriolis couplings. This range of partial waves gives converged ICSs and DCSs for collision energies up to 0.1 \(eV\). Calculations required \(8 \times 10^5\) iteration steps to converge which has been verified through calculations employing up to \(2 \times 10^5\) iteration steps.

B. Quasiclassical trajectory method

The general methodology of the QCT calculation is the same as that used in our recent work on the \(\text{C} + \text{OH}\) (Ref. 2) and \(S + \text{OH}\) (Ref. 19) systems. It has been extensively

FIG. 1. Schematic potential energy profile for the second excited \(^1A'\) surface of the \(\text{C}(^3P) + \text{OH}(^2\Pi) \rightarrow \text{CO}(^2\Pi) + \text{H}(^2S)\) reaction. Inversion barriers (I1 and I2) and saddle points (SP1, SP2, and SP3) are included. The energy diagrams for the two possible reaction pathways: (i) \(\text{C} + \text{OH} \rightarrow \text{COH} \rightarrow \text{SP3} \rightarrow \text{CO} + \text{H}\) and (ii) \(\text{C} + \text{OH} \rightarrow \text{COH} \rightarrow \text{SP1} \rightarrow \text{HCO} \rightarrow \text{SP2} \rightarrow \text{CO} + \text{H}\), are shown.

<table>
<thead>
<tr>
<th>Scattering coordinate ((R)) range</th>
<th>0.05–9.0</th>
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<tbody>
<tr>
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</tr>
<tr>
<td>Internal coordinate ((r)) range</td>
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<tr>
<td>Number of grid points in (r)</td>
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</tr>
<tr>
<td>Number of angular grid points</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Absorption strength in (R) ((r))</td>
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<tr>
<td>Centre of initial wave packet ((R_0))</td>
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</tr>
<tr>
<td>Width of the wave packet, (\sigma)</td>
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<tr>
<td>Smoothing of the wave packet, (\beta)</td>
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<tr>
<td>Analysis line, (R_{\infty})</td>
<td>6.35</td>
</tr>
</tbody>
</table>
described in Refs. 4 and 25 and we will give here only the particular details relevant to this study.

The QCT calculations used standard Monte Carlo sampling of the initial conditions and a step-adaptive Adams method to integrate the set of coupled Hamilton equations. We checked carefully the conservation of both the total energy and total angular momentum. At each integration step, we require a relative precision of $10^{-8}$ for the distances and for the momenta. The total energy was conserved to within $\pm 10^{-3}$ eV and the total angular momentum, to within $\pm 10^{-5} \hbar$. By calculating $1 \times 10^5$ trajectories the statistical Monte Carlo error in the integral cross sections was less than 0.5%.

Trajectories were started at a distance from the atom to the center-of-mass of the OH molecule of 12 Å at the highest collision energies and increased up to 21 Å at the lowest collision energy. The trajectories were halted when the recoil distance becomes larger than 10 Å and the recoil speed is quasi-constant. These values have been chosen to reduce any effect of long-range interactions. Preliminary batches of 500 trajectories were carried out at each collision energy to determine the maximum impact parameter $b_{\text{max}}$. This value ranges from 9.5 Å at the lowest energy down to 2.08 Å at the highest collision energy. Then batches of $1 \times 10^5$ trajectories have been run with the appropriate maximum impact parameter. To check the validity of this number of trajectories, we carried out additional calculations of cross sections for the C+OH($v = 0$, $j = 0$) reaction at a few translational energies with $2 \times 10^5$ trajectories. The results obtained with $2 \times 10^5$ trajectories were identical to those obtained with $1 \times 10^5$ trajectories.

C. Statistical methods

In this paper we have used the statistical quantum mechanical (SQM) method from Refs. 26 and 27. Details about its theoretical foundations and applications to the study of insertion and complex-forming reactions have been given elsewhere before (see, for instance, a review in Ref. 28), so here only a brief discussion of the relevant technical issues will be presented.

Within the assumption that the collision process proceeds via a complex-forming mechanism, the state-to-state reaction probability can be written as the product of the individual probability for the complex to be formed from an initial state by the fraction of complexes to fragmentate into products in the specified final state. Whereas ICSs are calculated from these estimations of the reaction probabilities, DCSs required the random phase approximation, as no information regarding the phase of the total scattering matrix is obtained in the present statistical context. Within such an approximation, the interference terms between different values of both the total angular momentum and the parity are neglected. Those terms arise from the coherent sums over the conserved quantum numbers, $J$ and $I$, respectively, in the expression for the exact QM DCS involving reactive scattering matrix elements rather than transition probabilities (the only quantities calculated in the statistical approach).

The SQM approach has been employed in its fully coupled-channel version with no approximation regarding the Coriolis coupling. However, the large number of rovibrational states of the CO($v'$, $j'$) products for the energies considered in the calculation ($v'_{\text{max}} = 7$ and $j'_{\text{max}} = 65$ at $E_c = 0.2$ eV) made us to consider separate runs of the model for limited sets of rotational states $j'$. In particular, we have divided the total range $[j_0, j_{\text{max}}]$ into the sequence $[0, 15], [16, 30], [31, 65]$. This procedure has been followed before for previous studies of the O($^1D$)+HCl (Ref. 29) and H+O$_2$ (Ref. 30) reactions. Its validity is tested by comparison with the full SQM calculation at selected values of $J$ and the collision energy of the corresponding individual capture reaction probabilities in the product CO+H arrangement. Table II shows such a comparison for the cases $E_c = 0.15$ eV, $J = 15$ and $E_c = 0.2$ eV and $J = 10$ for different values of the CO($v'$, $j'$) and the specific case of the helicity $\Omega' = 0$. The degree of agreement found is sufficiently good to justify the noticeable reduction on the computational effort.

In addition, we have employed a statistical method based in the propagation of QCT (SQCT) in a similar way as the recently proposed approach by Aoiz et al., which provide rather good results as compared with the SQM as reviewed for several systems. In our study, the method has been

<table>
<thead>
<tr>
<th>$E_c$</th>
<th>$(v', j')$</th>
<th>Full</th>
<th>Approx.</th>
<th>$(v', j')$</th>
<th>Full</th>
<th>Approx.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>(0, 0)</td>
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<td>0.3041</td>
<td>(0, 10)</td>
<td>0.2903</td>
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<tr>
<td></td>
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<td>(1, 10)</td>
<td>0.1530</td>
<td>0.2143</td>
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<tr>
<td></td>
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<td>0.0100</td>
<td>(2, 10)</td>
<td>0.0121</td>
<td>0.0215</td>
</tr>
<tr>
<td></td>
<td>(3, 0)</td>
<td>$2 \times 10^{-5}$</td>
<td>$2 \times 10^{-5}$</td>
<td>(3, 10)</td>
<td>$3 \times 10^{-5}$</td>
<td>$8 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.2 eV; $J = 10$</td>
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<td>1.0000</td>
<td>(0, 10)</td>
<td>0.3376</td>
<td>0.4472</td>
</tr>
<tr>
<td></td>
<td>(1, 0)</td>
<td>0.1523</td>
<td>0.1730</td>
<td>(1, 10)</td>
<td>0.1865</td>
<td>0.2593</td>
</tr>
<tr>
<td></td>
<td>(2, 0)</td>
<td>0.0151</td>
<td>0.0170</td>
<td>(2, 10)</td>
<td>0.0794</td>
<td>0.1063</td>
</tr>
<tr>
<td></td>
<td>(3, 0)</td>
<td>0.0002</td>
<td>0.0002</td>
<td>(3, 10)</td>
<td>0.0015</td>
<td>0.0021</td>
</tr>
</tbody>
</table>
applied for the $J = 0$ case, with different possible constraints to calculate the capture probabilities on the entrance channel.

In case 1 (SQCT1), one trajectory is considered as “captured” provided that it reaches a region in which the potential energy is smaller than a certain quantity, typically 0.125 eV, below the corresponding value at the asymptotic region, either reactants or products, depending on the arrangement in which the propagation is performed. Interestingly, the analysis of the average C–O, O–H and C–H interparticle distances found for the trajectories at the moment of being stopped, enabled us to define the values of the capture radii for the above discussed SQM calculation. For the present case, the time-independent propagation of the SQM method was carried out between 1.3 Å and the C+OH asymptotic region for the entrance channel and between 1.9 Å and the CO+H asymptote for the product channel.

A second requirement imposed to trajectories (SQCT2), in addition to the value of the potential energy discussed above, regards the value for the O–H distance, which is forced to be larger than 2 Å. Despite this condition favours the contribution from trajectories exploring the second well, associated to the HCO species, given the exothermicity of the reaction, the possibility of contribution from those cases leading directly to the products channel from the entrance arrangement is not discarded.

In case 3 (SQCT3), the potential energy condition is set to 0.65 eV with the same restriction over the O–H distance. Thus, we ensure that only those trajectories reaching the second well contribute to the capture probability in the reactant channel. For the three different cases, the capture probabilities are calculated as the ratio between the number of trajectories satisfying the corresponding requirements and the total number of trajectories run in the calculation ($10^5$ for each energy and initial state of reactants or products).

### III. RESULTS

#### A. Energy diagrams and reaction pathways

Our study of the $\text{C}(^3P)+\text{OH}(X^2\Pi) \rightarrow \text{CO}(a^3\Pi)+\text{H}(^2S)$ reaction begins with an analysis of the main features existing on the second excited $^1A''$ surface and their possible influence on the global dynamics of the process. A schematic diagram with energy paths, inversion barriers for the COH and HCO potential minima, indicated as I1 and I2, respectively, and the different saddle points, already mentioned in the Introduction, are shown in Fig. 1. In view of the topology of the PES, two possible reaction pathways are available. Once the COH minimum is reached, the course of the process can follow either the direct pathway via the SP3 saddle point before getting to the product arrangement, or, alternatively, to proceed by crossing the SP1 saddle point towards the HCO potential well and then, leads to products through the SP2 saddle point.

These two reaction mechanisms, the direct $\text{C}+\text{OH} \rightarrow \text{COH} \rightarrow \text{SP3} \rightarrow \text{CO}+\text{H}$, and the sequential pathway $\text{C}+\text{OH} \rightarrow \text{COH} \rightarrow \text{SP1} \rightarrow \text{HCO} \rightarrow \text{SP2} \rightarrow \text{CO}+\text{H}$, are also evident from the cuts of the PES shown in Fig. 2. On its left panel the surface is represented with Jacobi coordinates for the C+OH reactants, with a fixed O–H distance of 0.97 Å. From the figure it becomes evident that at the entrance channel, the COH minimum is the only accessible potential well. As indicated by the arrows included in Fig. 2, once the COH species is reached, it is possible to find some nonreactive backward flux which leads again to the C+OH reactants. However, it is via the SP1 saddle point that the reaction may follow the above-mentioned sequential pathway which involves the exploration of the HCO potential minimum. This route is shown in the right panel of Fig. 2, where the cut of the surface has been constructed with the Jacobi coordinates for the product arrangement. The C–O distance is fixed to 1.40 Å.

![Contour plots the $^1A''$ PES in terms of the $R$ and $\theta$ Jacobi coordinates for the reactant (left panel) and product (right panel) arrangements.](image-url)
From the COH minimum the direct pathway involves to overcome the 0.03 eV (measured from the C+OH channel) of the SP3 saddle point. The preference for one or the other way is further analysed below.

## B. Reaction probabilities

The reaction probability for a zero angular momentum \( J = 0 \) in the collision energy range up to 0.8 eV is presented in Fig. 3. The profile of the present TDWP reaction probability (black line) exhibits a large number of narrow resonances, which are of larger intensity at low energies. The overall behaviour differs from the reaction probability obtained on the ground electronic state at \( J = 0 \), which was found to be almost the unity for the entire energy range.\(^5\) The TDWP probabilities are in a rather good agreement with results reported in the TiQM study by Jorfi and Honvault\(^7\) (not shown here) despite not all the resonance peaks match perfectly.

QCT reaction probabilities for the title reaction were already reported in Ref. 7, but are also included here (green line) for the sake of comparison in Fig. 3. These values provide an average description of the QM probabilities, despite the absence of the narrow peaks associated with possible resonances. The SQM \( J = 0 \) results, on the other hand, exhibit an intriguing behaviour, clearly above the TDWP and QCT probabilities, with a minimum at \( E_c \sim 0.05 \) eV. Beyond that energy a monotonically raise seems to stabilize in a plateau for \( E_c > 0.4 \) eV.

It is by means of the three different cases under consideration for the SQCT approach discussed in Sec. II C, that we can understand the origin of such discrepancies between the SQM result and the TDWP probabilities. When we only impose an energy restriction to count trajectories for the calculation of the capture probabilities (SQCT1 case in blue dashed line in Fig. 3) the result displays a quite similar trend with respect to the statistical prediction in its QM version. The quantitative agreement between the SQCT1 and SQM probabilities is noticeable as shown in Fig. 3, in which the energy range has been extended with respect to the TDWP calculation to analyze the trend followed by the two statistical results.

SQCT2 and SQCT3 calculations (blue dotted and solid lines, respectively, in Fig. 3) in turn yield probabilities in line with the results from the QCT and TDWP methods. Moreover, the accord found in Fig. 3 between both statistical methods indicates that the reaction proceeds mainly via a complex-forming pathway in the HCO well with few contribution from a direct mechanism with no visits to this specific second well. The role played by this latter reaction pathway accounts for the slightly larger probability exhibited by the SQCT2 reaction probabilities in comparison with the SQCT3 result.

A deeper insight regarding the precise course of the reaction can be obtained from the analysis of the trajectories propagated in the complete QCT calculation. Thus, it is possible to investigate the reaction probability as a function of the energy for any value of the impact parameter \( b \) separating the contribution from different sets of trajectories. Figure 4 shows such total reaction probability with all trajectories considered in the calculation and separate contributions according to the precise region of the potential explored: (i) the first potential well associated to the COH species (in green); (ii) the potential well associated to the HCO species (in blue); and (iii) trajectories exploring both wells (in red). The comparison of the different probabilities reveals that the process involves the visit to the two potential minima (the above discussed C+OH \( \rightarrow \) COH \( \rightarrow \) SP1 \( \rightarrow \) HCO \( \rightarrow \) SP2 \( \rightarrow \) H+CO pathway), with a negligible contribution of processes occurring solely via the HCO well (the direct C+OH \( \rightarrow \) HCO \( \rightarrow \) SP2 \( \rightarrow \) H+CO route). This result thus confirms that the topology of the entrance channel drives the C atom to the COH well directly with no possibility of a direct path to the HCO well.
The calculation of reaction probabilities has been extended to nonzero values of the total angular momentum. TDWP results up to $J = 50$ were calculated for an energy range of 0.4 eV. In Fig. 5, we present the $J = 10$ (bottom panel), $J = 30$ (mid panel), and $J = 40$ cases (top panel). The structure of intense and narrow peaks seen for $J = 0$ at very low energies is progressively disappearing as $J$ increases. The onset of a threshold for reaction due to the presence of centrifugal barriers associated with the increasingly larger values of the total angular momentum is also evident from the figure.

The corresponding SQM predictions, also included in Fig. 5, suffer an interesting evolution when $J$ is increased. For $J = 10$, the statistical probabilities remain above the TDWP result, specially at the lowest energies. The overall oscillations seen in the exact probabilities seem to be followed in average by the SQM estimates. For $J = 30$, the threshold is correctly reproduced and the differences regarding the intensities of both set of probabilities is certainly reduced. It is, however, for $J = 40$ that the SQM results become a decent reproduction of the TDWP probabilities.

A further investigation on the performance of some of the theoretical methods employed in the present study for $J > 0$ can be carried out by comparing the corresponding reaction probabilities at specific values of the collision energy. In Fig. 6, we show the cases for $E_c = 0.05$ eV (bottom panel), 0.1 eV (mid panel), and 0.2 eV (top panel). The comparison in this figure confirms the good accord found between the QCT probabilities and the TDWP results. The SQM predictions on the contrary are always above the exact probabilities almost for all values of the total angular momentum, with a slight improvement when $J$ is large, consistent with the observed trend in Fig. 5.

### C. Integral cross sections

Total ICSs have been calculated by means of the TDWP, QCT, and SQM methods. The comparison between the corresponding results in terms of the collision energy is shown in Fig. 7. As in the case of the ground electronic state, the profile of the cross section corresponds to the typical barrierless reaction with a marked and steep decrease below $E_c \sim 0.2$ eV and a progressive stabilization around a plateau value as the energy increases. The TDWP cross section is shown as a solid black line, the SQM results are represented by red squares connected by a red line, and the QCT approach is indicated by blue circles.

![FIG. 7. ICSs (in Å²) in terms of the collision energy for the C+OH reaction obtained by the TDWP (black line), SQM (red squares and line), and QCT (blue line) approaches. The vertical dashed line shows the energy range of convergence for the TDWP result.](image-url)
sections are converged up to a value of the collision energy of \( \sim 0.1 \) eV (as indicated in Fig. 7 with a vertical dashed line). Thus beyond that energy, the corresponding ICSs can be considered only as approximative. The values of the ICSs obtained by means of the QCT approach are in a good agreement with the TDWP results with the only exception of the calculation performed at \( E_c = 0.01 \) eV. It might be assumed that the missing contribution from more \( J \) partial waves for \( E_c > 0.1 \) eV would yield slightly larger TDWP cross sections with respect to the QCT results, as observed at the lower energy range. The statistical predictions calculated with the SQM approach are above the exact results. This was nevertheless an expected result considering the over-estimation observed for the reaction probabilities for some values of \( J \) as shown in Sec. III B. The interesting thing is that, despite this quantitative discrepancy, the SQM cross sections exhibit the same trend in terms of the collision energy as the QCT and TDWP results. The progressive improvement found for the largest partial waves (see \( J = 40 \) in Fig. 5) could possibly be responsible for the good qualitative behaviour.

The comparison has been extended for final vibrational state selected cross sections at specific values of \( E_c \). Table III shows these ICSs for the CO(\( v' = 0 \)) states at selected collision energies between 0.01 eV and 0.1 eV. The main source of discrepancy between the SQM and TDWP results comes from the population of CO formed in its vibrational ground state \( v' = 0 \). The statistical values are about two times larger than the exact distributions. The agreement is, on the contrary, remarkable for the cross section of the C+OH \((v = 0, j = 0) \rightarrow \text{CO}(v' = 1) + \text{H}\) reaction. The population of the CO(\( v' = 2 \)) state is almost negligible for all energies according to both theoretical methods. The QCT results included in Table III, reduced to \( E_c = 0.01 \) eV and \( E_c = 0.05 \) eV, show the good performance of such method for the larger energy.

### D. Differential cross sections

Another source of useful information regarding the dynamics which govern the reaction are the DCSs. In this work we have employed the TDWP method to calculate accurate QM cross sections for a range of values for the collision energy between 0.01 eV and 0.1 eV. A color map of these DCSs as a function of \( E_c \) is shown in Fig. 8. The angular distributions are found to decrease as we consider larger values of the collision energy and the apparent preference for the forward \((\theta \sim 0^\circ)\) and backward \((\theta \sim 180^\circ)\) scattering angles seems to be much more noticeable at the low energy regime.

This trend is confirmed in Fig. 9 when DCSs at two specific values of \( E_c \) are plotted. In particular the TDWP results are compared at the top panel of the figure at 0.05 eV and 0.1 eV. The cross sections for the lowest of the energies under consideration \((E_c = 0.05 \text{ eV})\) is larger than the other case. The DCSs shown in the figure display a symmetric forward-backward profile, a feature which is usually assigned to reactions proceeding via a complex-forming mechanism.\(^{34, 35}\) as suggested by the participation of the two deep wells of the PESs in the overall dynamics. The QCT results, shown in the mid panel of Fig. 9, present a remarkable agreement with the TDWP results, specially at the vicinity of the sideways region \((\theta \sim 90^\circ)\) although the marked preference for the peaks of the forward and backward scattering directions of the DCS at \( E_c = 0.05 \) eV is not completely well reproduced.

This feature observed in the exact angular cross sections is thus consistent with the preference of the trajectories to visit the existing potential wells associated to the COH and HCO species in their route to products. However, the SQM approach is not capable to reproduce the TDWP results. On one hand, the statistical cross sections are clearly above the exact values, in line with the overestimation found for both reaction probabilities and ICSs, and, on the other hand, the ratio between the cross sections through the forward-backward peaks and through the sideways scattering at \( E_c = 0.05 \) eV, is too large in comparison with the results of the TDWP calculation. The value of such a ratio in the

### TABLE III. Final vibrational state resolved ICS in Å² for the C+OH \( \rightarrow \text{CO}(v' = 0 \rightarrow 2) + \text{H} \) reaction obtained by means of the TDWP, SQM, and QCT methods.

<table>
<thead>
<tr>
<th>( E_c ) (eV)</th>
<th>TDWP</th>
<th>SQM</th>
<th>QCT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \sigma_{v' = 0} )</td>
<td>( \sigma_{v' = 1} )</td>
<td>( \sigma_{v' = 2} )</td>
</tr>
<tr>
<td>0.01</td>
<td>35.60</td>
<td>7.99</td>
<td>0.70</td>
</tr>
<tr>
<td>0.02</td>
<td>16.62</td>
<td>3.50</td>
<td>0.32</td>
</tr>
<tr>
<td>0.03</td>
<td>10.39</td>
<td>2.33</td>
<td>0.22</td>
</tr>
<tr>
<td>0.05</td>
<td>6.29</td>
<td>1.40</td>
<td>0.14</td>
</tr>
<tr>
<td>0.1</td>
<td>2.53</td>
<td>0.71</td>
<td>0.10</td>
</tr>
</tbody>
</table>
features observed in the exact TDWP and QCT calculations. The SQM method fails to reproduce satisfactorily the main
rects the HCO with a multi-well structure (see, for instance, the cases of the
Si+O_2 (Ref. 37) and O+HCl (Ref. 29 and 38) reactions), the SQM method fails to reproduce satisfactorily the main features observed in the exact TDWP and QCT calculations for the C+OH reaction. The origin of such deficiencies may arise nevertheless from the specific nature of the PES which displays a saddle point which seems to separate resonances associated with each potential wells, a barrier for the CO–H dissociation from the COH well and a saddle point which directs the HCO → CO+H final step (the SP1, SP2, and SP3 saddle points, respectively). The QCT analysis has revealed in fact a rich variety of processes linked to this double well structure and saddle points which forces the reaction to follow different possible routes. For instance, once in the COH well, the first minimum after the reactants entrance, where the C–O equilibrium distance is about 1.4 Å, an energy of ~0.45 eV with respect to reactants is required for the complex to evolve in a direct process to products. Such a transition would be nevertheless possible with a noticeable reduction of the C–O distance down to 1.2 Å (Ref. 2) with the corresponding barrier to CO+H decreasing down to 0.03 eV, the SP3 saddle point.

One could reason in terms of these changes in the interparticle distances required for an efficient crossing of the saddle points existing in the PESs to understand the differences observed in the statistical prediction of the CO(v′ = 0) final population with respect to the TDWP value. Discrepancies which seems to disappear however when we analyse the formation of CO(v′ = 1) (see Table III). Thus, given the difference between the classical turning points in the diatomic potential curves for the v′ = 0 and v′ = 1 states, the above mentioned reduction of the C–O distance to overcome the SP3 barrier could be, in principle, more easily accomplished for a vibrationally excited CO fragment than in its vibrational ground state. This apparent advantage of the excited case, with a C–O vibration which can stretch to smaller minimum distances and therefore to find more favourable cases to cross the saddle point to products, does not yield however to an inversion of the final vibrational population of the CO diatom, but could be enough to explain the failure for the cross sections of the CO(v′ = 0) production in the statistical approach, which would account for more reactive cases than in the exact calculation.

Alternatively, the barrier between the two isomers COH and HCO acts as a bottleneck, separating thus resonances associated to each potential well. Visits to the COH potential minimum might end up with reaction flux reflected back to reactants which would not play any role in the final reactivity. Their contribution is not either included in the statistical estimates performed right at the entrance of the potential well. The situation is also subtle at the HCO well, for which, possible trapped trajectories have to overcome the saddle point of about 0.11 eV below the C+OH asymptote but about 0.3 eV above the products channel. A correct description of the capture radius at that region is also mandatory to describe the dynamics just before reaching the products. In this sense, the flexibility of the SQCT approach in order to maintain the propagation of the trajectories somehow further than the strict requirements imposed at the entrance of both reactants and products arrangements within the SQM method enables a better understanding of the overall mechanisms governing the process.

The apparent capability exhibited by the SQM approach to reproduce reaction probabilities at large values of J nevertheless constitute a noticeable improvement for such a desired description. In addition, the analysis of both reaction probabilities and ICSs (see Figs. 6 and 7, respectively) reveals that the complex-forming nature of the process enables the statistical technique to become adequate as the energy increases.

![FIG. 9. Comparison of DCSs obtained by means of the TDWP (top panel), QCT (mid panel), and SQM (bottom panel) methods at two values of the collision energy: E = 0.05 eV and 0.1 eV.](image-url)
It is worth mentioning that the present TDWP results constitute the first report of accurate calculations for the title reaction for nonzero total angular momenta. One of the main advantages in this respect of the second excited surface, $1^4A''$, in comparison with both the first excited, $1^2A''$, and the ground state, $X^2A'$, is the difference in the depth of the existing potential minima already discussed in Sec. I. That explains the use of different approximations in such cases to treat the $J > 0$ situations. It would be of great interest to investigate the reliability of a similar calculation in these two other reactions, in order to establish a deeper insight of the possible differences in the dynamical mechanisms on different electronic states.

V. CONCLUSIONS

The C($^3P$)+OH($^3Π$) $\rightarrow$ CO($^3Π$)+H($^3S$) reaction has been studied on the excited $1^4A''$ electronic state by means of an accurate quantum mechanical method in combination with quasi-classical trajectory and statistical techniques. Reaction probabilities, integral cross sections, and differential cross sections have been calculated to analyze the dynamics of the process. A marked resonance structure with numerous narrow peaks and the observed forward-backward symmetry in the differential cross sections suggest the occurrence of a complex-forming mechanisms. This possibility is nevertheless not fully accounted for by a statistical quantum method which fails to describe the role played by the existing two potential wells for the process. The quasi-classical trajectory approaches employed in the study reveal the importance of a correct description of the reaction pathway involving these minima associated with the COH and HCO species.

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