Quasiclassical trajectory and statistical quantum calculations for the $\text{C} + \text{OH} \rightarrow \text{CO} + \text{H}$ reaction on the first excited $1^2\text{A}''$ potential energy surface

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Abstract

We report quasiclassical trajectory dynamical calculations for the $\text{C}(^3P) + \text{OH}(X^2\Pi) \rightarrow \text{CO}(a^3\Pi) + \text{H}(^2S)$ using a recently developed *ab initio* potential energy surface for the first electronic state of HCO of $1^2\text{A}''$ symmetry. The dependence of integral cross sections on the collision energy is determined. Product energy and angular distributions have also been calculated. Integral cross sections show no energy threshold and decrease as the collision energy increases. The comparison with results obtained from a statistical quantum method seems to confirm that the reaction is mainly dominated by an indirect mechanism in which a long-lived intermediate complex is involved.

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I. INTRODUCTION

Radical-radical reactions involving the collision of OH with a C, N, O or F atom can play a crucial role in the chemistry of planetary atmospheres and interstellar medium. Their experimental study is nevertheless not easy, and only recently it has been possible to investigate the reaction kinetics of processes such as N+OH [1] in some detail. Theoretical calculations for this process [1] for instance have provided insights about the dynamics which rule these reactions. For the C+OH case, on the contrary, no measurements have been reported up to date. Theoretical studies are therefore needed in order to predict the features of this reaction and to understand its mechanisms. Accurate quantum-mechanical (QM) studies are sparse for these reactions due to the presence of deep wells in the corresponding potential energy surfaces (PESs) which characterise the collision.

Most dynamical studies about the C + OH system concern the $C(^3P) + OH(X^2\Pi) \rightarrow CO(X^1\Sigma^+) + H(^2S)$ reaction on the X^2A' ground state PES. The excitation function, state-specific and thermal rate constants for this reaction have been calculated in the 1 - 500 K temperature range by means of quasi-classical trajectory (QCT) calculations [2] on the global PES built by Zanchet *et al.* [3]. The maximum of the thermal rate constant value is $3.39 \cdot 10^{-10} \text{ cm}^3\text{s}^{-1}$ at 7 K. In addition differential cross sections (DCSs), product vibrational, rotational and translational distributions have also been determined [4] for different rovibrational states of OH and for several collision energies E_c . The QCT results have shown that the reaction on the ground state PES is mainly dominated by a direct mechanism in which a very-short lived intermediate complex is involved. The process was found to obey the $H + HL \rightarrow HH + L$ (with H for Heavy and L for Light) kinematic constraint which implies an almost total conversion $\mathbf{L} \rightarrow \mathbf{j}'$ [4, 5], where $\mathbf{L}$ is the initial orbital angular momentum and $\mathbf{j}'$ is the product rotational angular momentum. Indeed, the reactant reduced mass, μ_{C-OH} , is approximately 7 times that of the products, μ_{H-CO} . Consequently, $L \gg L'$. Since the modulus of $\mathbf{j}$ is usually much smaller than the modulus of $\mathbf{L}$, conservation of the total angular momentum $\mathbf{J}$ implies that $\mathbf{L} \sim \mathbf{j}'$.

Exact (for a zero total angular momentum $J = 0$) and statistical time-dependent wave packet (TDWP) calculations [6, 7] have been carried out on the ground state PES. The calculated quantum ICS and rate constants are in good agreement with the QCT results, except at temperatures below 100 K. The calculated TDWP and QCT excitation functions

decrease with increasing E_c , as expected for an exothermic barrierless reaction. The state-selected rate coefficients are practically insensitive to temperature, with the exception of the low temperature region. An overall good agreement was seen with the corresponding QCT results above 100 K, with the results reported in Ref. [6] and those obtained by means of two different statistically-based methods, the adiabatic capture centrifugal sudden approximation and the mean potential capture theory employed in Ref. [8]. This latter study tested the sensitivity of the rate coefficients with the long range part of the PES and revealed that the entrance channel plays a major role, another expected result for a reaction mediated by the absence of any barrier in the PES.

There exist two other electronic states, $1^2A''$ and $1^4A''$, which correlate to $C(^3P) + OH(X^2\Pi)$ as the ground state, but to an excited state of the products leading to $CO(a^3\Pi) + H(^2S)$. Recently, some of us have performed high level *ab initio* calculations [9] for the first four excited states, $1^2A''$, $1^4A''$, $2^2A'$ and $1^4A'$, at the multireference internally contracted single and double configuration interaction (MR-SDCI) level corrected for its size-inconsistency by the Davidson method. At low E_c , the $2^2A'$ and $1^4A'$ states are not involved in the $C + OH$ reaction as they exhibit a strong repulsive behaviour. On the contrary, the $1^2A''$ and $1^4A''$ states present no barrier along the reaction path. Global PESs have therefore been built up for the $1^2A''$ and $1^4A''$ states only, using the reproducing kernel Hilbert space method [10]. Thermal rate constants have then been computed on the two PESs using a QCT method [9]. In the present work, we are interested in the first excited electronic state $1^2A''$.

The $1^2A''$ state PES presents no entrance barrier as the X^2A' ground state. Two minima located energetically above those of the ground state have been found. Figure 1 (upper panel) shows the HCO global minimum and the COH secondary minimum, as well as the saddle point associated to the isomerisation barrier between the two conformations. This first excited electronic state has an exoergicity $\Delta H_0^0 = -0.41$ eV [9], which is much smaller than the one of the ground state (6.5 eV).

The topology of the second excited $1^4A''$ PES, characterised by a similar double well structure and numerous saddle points, plays a crucial role in the dynamics of the $C + OH$ reaction. The competition of two pathways, one involving the exploration of the entrance potential well COH and the sequential route in which both the COH and HCO minimum wells are explored, has been analyzed by means of TDWP, QCT and statistical methods [11].

Reaction probabilities, integral and DCSs were calculated and, despite the deficiencies of the statistical quantum method (SQM) to give account for the successive passages through the existing saddle points, a complex-forming process was suggested as the leading mechanism. For the case of the first excited state $1^2A''$ PES investigated here, it is interesting to analyze if different pathways associated to each potential well also compete in the overall dynamics of the process.

All the three PESs mentioned above present two deep potential wells, and the main difference between the ground state and the two first electronic states is the value of the exoergicity. The absence of the resonance peaks in the reaction probabilities on the ground state, X^2A' , is explained on the basis of high exoergicity (6.5 eV) of the reaction. The high exoergicity makes the product channels accessible and hence results in the faster decay of the resonances. In contrast, the reaction on the first ($1^2A''$) and second ($1^4A''$) excited PESs have very low exoergicity (0.41 eV) and hence the resonances have a longer lifetime and are observed in the reaction probabilities. In Ref. [9], using QCT calculations we have given the relative contributions of the different PESs to the reactivity. As expected, the exoergicity being much smaller on the excited states than on the ground state, the rate constants computed on the excited PESs for temperatures T between 10 K and 500 K are significantly lower than the rate obtained on the X^2A' PES, by a factor which varies between 2 (for $T > 40$ K) and 7 (at $T = 10$ K). The total thermal rate constant is therefore close to the ground state rate at low temperatures. However, above 20 K, both the $1^2A''$ and $1^4A''$ PESs significantly contribute to the total rate constant.

In a recent paper total reaction probability, vibrationally and rotationally product state-resolved reaction probabilities, vibrational and rotational product distributions at $J = 0$ have been calculated for the $C(^3P) + OH(X^2\Pi) \rightarrow CO(a^3\Pi) + H(^2S)$ reaction on the $1^2A''$ state PES using a time-independent quantum-mechanical (TIQM) method [12]. The total reaction probability was found to show a dense resonance structure in the collision energy range from 0 to 0.9 eV attributed to long-lived resonances supported by the HCO/COH potential wells. The rate constant was computed by means of a J -shifting approach [8] and a good agreement with the QCT prediction [9] was observed. The TIQM results confirmed that the dynamics on the $1^2A''$ first excited state is totally different from that on the X^2A' ground state. However, accurate QM calculations for $J > 0$ remains computationally extremely expensive today for such a system, and the QCT and statistical techniques offer an

interesting alternative to QM methods to probe the dynamics of the process.

The study of non-adiabatic effects for the C + OH reaction goes beyond the scope of the present manuscript and so they are neglected here. The non-adiabatic effects have been described in detail in Ref [9] and in a next step the couplings between the different PESs, especially the $X^2A'-1^2A''$ Renner-Teller coupling, should be computed and incorporated in a multisurface dynamical treatment.

In this work we investigate the dynamics of the title reaction by means of QCT and SQM calculations. Reaction probabilities, ICSs and DCSs obtained by means of both methods are compared. The structure of the paper is as follows: In Section II numerical and theoretical details of both calculations are given; in Section III results are presented and discussed and finally in Section IV we list the main conclusions.

II. THEORETICAL METHODS

A. Quasiclassical trajectory calculations

Reaction probabilities, ICSs, DCSs and rate constants have been calculated using the QCT code developed by Halvick and Rayez [13]. The QCT method is presented in detail in Ref. [2]. Only the specific features to the present calculations are mentioned in the following text.

A standard Monte Carlo sampling of the initial conditions has been used and the set of Hamilton equations have been integrated using a step adaptive Adams method. Both the total energy and angular momentum are well conserved during the reaction with an average error of 10^{-4} eV and 10^{-5} $\hbar$ respectively. The carbon atom is initially separated from the center-of-mass of OH by 10 Å for the highest E_c and 20 Å for the lowest ones. At 10 Å long range interaction are negligible and the trajectories are stopped when the recoil distance is larger than this value. To optimize the sampling of the impact parameter, preliminary tests with a few trajectories (about 500) were performed. Then we have run batches of 100 000 trajectories with the appropriate value of the maximum impact parameter which varies from 9.7 Å at 1 meV to 3.2 Å as energy increases. This leads to a small statistical Monte Carlo error, around 0.2%. In addition, a few batches with a number of trajectories which varies from 5000 to 200 000 have been performed, in order to check that the results obtained

with 100 000 trajectories are well converged.

All the results presented below have been obtained for the $\text{C}(^3P) + \text{OH}(X^2\Pi, v = 0) \rightarrow \text{CO}(a^3\Pi) + \text{H}(^2S)$ reaction on the $1^2A''$ PES.

B. Statistical quantum method

The statistical results presented in this paper have been obtained with the SQM method developed by Manolopoulos and coworkers [14, 15]. This approach has been explained in detail before (see for example Ref. 16 for a previous review and Refs. [17–20] for some of the most recent applications).

Within this approach, the state-to-state probability is approximated by the product of the individual capture probability for the complex to be formed from the initial state and the fraction of such intermediate species which finally fragmentate into the final state. The capture probabilities are obtained by solving the corresponding coupled-channel equations by means of a log derivative method between the region defined between a capture radius, R_c and the asymptotic region. The calculation of the DCS requires to invoke the random phase approximation since the method only obtains the square modulus of the scattering matrix (see Ref. [15] for specific details).

The SQM approach has been applied in its centrifugal-sudden (CS) version where all the corresponding Coriolis couplings (CC) are neglected. This approximation was suggested to be correct for the title reaction in the capture studies performed by Lin *et al.* on the ground PES [6] due to the choice of the C-OH Jacobi vector R in the reactant channel close to the least inertia axis. The noticeably smaller depth of the existing potential wells in the case of the second excited PES $1^4A''$ enabled a proper treatment of the CC without a extremely expensive computational cost. This is not however the case for the ground and first excited PESs. The capture radii are those considered as well for the statistical calculation performed in the $1^4A''$ surface [11]. Thus, R_c was chosen as 1.3 Å for the reactant channel and 1.9 Å for the product channel.

III. RESULTS AND DISCUSSION

A first deep insight regarding the precise course of the reaction can be obtained from the analysis of the trajectories propagated in the complete QCT calculation. A great advantage of the QCT approach is that the trajectories allow to explore the different regions on the PES. Thus it is possible to investigate the reaction probability as a function of the energy for any value of the impact parameter b_{max} separating the contribution from different sets of trajectories. Figure 2 shows such total reaction probability, $\langle P_r \rangle = N_r/N_{tot}$ (N_r and N_{tot} denote the number of reactive and total trajectories respectively), 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, with a negligible contribution of processes occurring solely via the HCO well or via the COH well.

An analogous analysis performed on the second excited PES $1^4A''$ [11] reveals differences with respect to the precise profile of the QCT reaction probabilities in terms of the energy but concedes a similar importance of the pathways which involve the exploration of both potential wells. The mechanism mediated solely by the COH minimum however was seen to play certain role in the process occurring on the second excited, a feature which is completely absent for the case of the ground PES investigated here.

Figure 3 shows the total reaction probability at $J = 0$ as a function of the collision energy E_c . The absence of barrier in the PES for the C + OH entrance arrangement leads to a total reaction probability which has no energy threshold. The reaction probability is high (up to 0.8) at very low energies and relatively small for $E_c > 0.5$ eV with an average value of 0.2. An extremely dense resonance structure is present in the TIQM reaction probability that was computed in a previous work [12]. These quantum-mechanical resonances are associated with a long-lived intermediate complex formed in the deep HCO/COH wells of the PES which supports many quasi-bound states. The QCT approach produces a fairly good average description of the quantum reaction probabilities, with a slight underestimate for $E_c > 0.2$ eV. However, the most striking feature shown in Fig. 3 is the SQM prediction. While no resonances are obtained using the SQM method as expected, because of an energy

average involved in the method, it is clear that the SQM reaction probability at $J = 0$ is not in accord with the QCT and TIQM results. However, the SQM prediction at $J = 0$ does not preclude to have a better agreement for cross sections. Indeed, a good agreement is found between the SQM result and the QCT prediction for the total ICS in magnitude and in dependence on the collision energy (See Fig. 4).

The dependence on E_c of initial state-selected ICSs (i.e. the excitation functions), $\sigma(E)$ computed for some rotational states of OH($v = 0$) are displayed in Fig. 4. The ICSs are noticeably large at low energies and decrease with increasing energy. This result is consistent with total reaction probabilities with no energy threshold [12], barrierless reactions with no specific features in the entrance channel which might conditionate the course of the process. The results hardly depend on the initial excitation of OH and the cross sections seem to follow roughly the order $\sigma(j = 1) < \sigma(j = 0) < \sigma(j = 5)$ on the whole energy range. It could be argued that results shown in Fig. 4 exhibit nevertheless some differences depending on the rotational excitation of the reactants in comparison with the almost complete absence of any signal of effect on the ICS due to different values of j for the ground state PES [2]. In Fig. 4 results obtained with the SQM have also been included for comparison. The values of the statistical prediction at specific values of the collision energy are in good agreement with the QCT ICS, a result which suggests the occurrence of a complex-forming mechanism during the course of the reaction.

Figure 5 shows the product vibrational distributions, i.e. the ICS as a function of the vibrational state v' of CO, at specific values of E_c between 0.01 and 0.5 eV. In all cases, the shape of the vibrational distributions is the same: the most populated vibrational level is $v' = 0$, with a regular decrease with v' which reflects the diminution of open rotational states in a given vibrational manifold. This behaviour is rather statistical as manifested by the comparison with the SQM cross sections, also included in the figure, and may be a feature of a complex-forming reaction. Apart of some overestimation of the cross section for the formation of vibrationless CO, specially at $E_c = 0.01$ eV and 0.05 eV, QCT and SQM results are in a reasonably good agreement. This behaviour with respect to the final vibrational state is in sharp contrast with the C + OH reaction on the ground state PES [4] where a strong vibrational population inversion was found for the same range of energy suggesting a direct mechanism. Another difference is that for the ground state PES case, the maximum value of v' , v'_{max} , is much higher (~ 24), due to the very large exothermicity as shown in

Fig. 1 (lower panel). Of course, as expected from Fig. 4, the vibrationally state-resolved ICS decreases with E_c .

The product rotational distributions, i.e. the ICS as a function of the rotational state j' of $\text{CO}(v')$, at four E_c are shown in Fig. 6. The magnitude of state selected ICSs decreases as v' increases, as expected from Fig. 5. Each product vibrational state distribution presents bell-shaped curves. The ICS increases regularly with j' , reaches a maximum at an intermediate j' and decreases to negligible values before reaching the last states accessible given by the energy conservation but also by momentum conservation as expected for a Heavy-Heavy-Light system. In such a case, the product rotational state is mostly controlled by the reactants angular orbital momentum and the kinematic constraint $\mathbf{L} \cong \mathbf{j}'$ is usually a good approximation as checked by the QCT results. Similar results were found for the $\text{C} + \text{OH}$ reaction on the ground state PES [4] and for the $\text{Li} + \text{HF}$ reaction [5]. The product rotational distributions are not very sensitive to E_c . However, for E_c below 0.1 eV, all the rotational states of CO contribute to the ICS, whereas at 0.5 eV only the medium and high rotational states of CO are significantly populated.

The comparison with the statistical predictions reveals a fairly good agreement at $E_c = 0.01$ eV and 0.5 eV, although differences with respect to highest available rotational state j' are noticeable for the lowest of the two energies. Some deficiencies are manifested in the SQM results for the two other energies under consideration, $E_c = 0.05$ eV and 0.1 eV. As opposed to the expected profile in a statistical distribution with increasing population of the corresponding rotational levels as j' increases and an abrupt decay once the highest rotational excitation of OH is reached, the cross sections exhibit an unusual maximum at an intermediate j' and an irregular profile afterwards. The most likely explanation lies in the poor performance of the CS approximation employed in the SQM calculation at that energy regime. Despite these differences with respect the QCT rotational distributions, the preceding comparisons with total and vibrationally-resolved ICSs manifest that the problems of the statistical predictions only arises at the most detailed state-to-state level.

Another indicator of the dynamics followed by the process are the DCSs. Figure 7 shows the total DCS for $\text{OH}(v = 0, j = 0)$ as a function of the center-of-mass (CM) scattering angle at 0.01, 0.05, 0.1 and 0.5 eV. The difference in magnitude reflects the one observed in total ICS. The shape of the angular distributions is nearly the same for all considered energies: forward-backward symmetry and sharp polarization peaks at 0° and 180° . This behaviour

may be a signature of a long-lived collision complex with a lifetime longer than one or more rotation periods. The average lifetime of the HCO/COH intermediate complexes is about 2000 fs at the four energies considered. Another indication of an indirect process is that there is no correlation between the impact parameters and the CM scattering angle at the four energies (not shown here) and all impact parameters contribute to forward, sideways or backward scattering. Moreover, we found that the average fraction of the total available energy in the product motion for rotation, vibration or translation, hereafter denoted $\langle f_r \rangle$, $\langle f_v \rangle$, or $\langle f_t \rangle$, does not depend on the CM scattering angle. However, the slight asymmetry found in DCSs suggests that some trajectories lead to short lifetime complex, not sufficiently long to render the reaction statistical. This indicates that direct reaction mechanism may occur on this PES, but that the reaction is mainly governed by insertion mechanism.

The comparison with the SQM predictions seems to confirm this suggestion. The agreement between the QCT and statistical DCSs all along the sideways ($\sim 90^\circ$) scattering region is remarkable at $E_c = 0.01$ eV, the lowest energy shown in Fig. 7. It is only at the forward and backward peaks where some differences are found, with the SQM cross section showing a much more pronounced preference than the QCT DCSs. For $E_c = 0.05$ eV and 0.1 eV the comparison reveals some overestimation of the SQM result, in line with the differences observed for the total ICS at those two energies (see Fig. 4). The trend of the angular cross sections for the sideways scattering region is similar for results obtained by means of both methods. The DCS obtained by means of the SQM method at $E_c = 0.5$ eV are not shown here because they are not correct due to deficiencies introduced by the CS approximation on the title reaction. The contribution coming from the largest values of the total angular momentum produces an artificial maximum around the sideways scattering direction. This feature enables us to suggest a limited validity for such treatment of the helicity components, which seems not to work as the collision energy is increased.

Same features are found for the vibrationally state-resolved DCSs displayed in Fig. 8. It is clear that all vibrational states of CO contribute to forward and backward scattering at all E_c , showing that the total DCS is not vibrationally specific. As for the product vibrational distribution (Fig. 5), no inversion population is found at each CM scattering angle and the $v' = 0$ vibrational state of CO gives the most important contribution to the total DCS. The SQM results, also included for comparison in Fig. 8, agree well with the QCT distributions. The shapes of the vibrationally state-resolved DCSs are similar and their absolute values

coincide to the extent of the agreement between the respective ICSs displayed in Fig. 5. Besides the fairly good agreement found at $E_c = 0.01$ eV, an expected result due to the comparisons shown before for rovibrational distributions, it is worth mentioning the good accord found with the QCT DCSs for the $\text{CO}(v' = 0)$ case at $E_c = 0.05$ eV and 0.1 eV. For these two energies, the total DCS obtained by means of the SQM is somehow larger than the QCT result. The comparison shown in Fig. 8 reveals that the source of discrepancy between both methods comes mainly for the cross section corresponding to vibrationally excited CO products, $v' > 0$. In all cases, the forward and backward peaks are less pronounced in the QCT results. The differences in forward/backward scattering between the SQM and QCT predictions can be explained by the neglect of parity in QCT calculations, as described in detail in Refs. [21] and [22].

Figure 9 presents the dependence on the collision energy of $\langle f_r \rangle$, $\langle f_v \rangle$, and $\langle f_t \rangle$ obtained from the QCT calculations. At medium and high collision E_c , the redistribution of the total available energy among the internal degrees of freedom of the complex and the translation motion of the products is almost independent on E_c . Above about 0.2 eV, $\langle f_r \rangle$, $\langle f_v \rangle$, or $\langle f_t \rangle$ keep constant values, 0.34, 0.22, 0.44 respectively. At low E_c (< 0.2 eV), $\langle f_r \rangle$ sharply increases with E_c while $\langle f_v \rangle$ decreases, $\langle f_t \rangle$ remains almost constant. For the whole energy range considered, the total available energy is preferentially transferred to translation. At low E_c , the strong enhancement of $\langle f_r \rangle$ can be attributed to the participation of progressively larger orbital angular momenta L . This is a consequence of the kinematic constraint associated with the combination of masses for the $\text{H} + \text{HL} \rightarrow \text{HH} + \text{L}$ reaction. As already mentioned, the well-known relation $\mathbf{L} \cong \mathbf{j}'$ is found for the title reaction. The increase of $\langle f_r \rangle$ with E_c therefore reflects the fact that the amount of rotation is mainly controlled by the reactants orbital angular momentum. However, at higher energy the maximum value of j' allowed by the orbital angular momentum is reached and $\langle f_r \rangle$ cannot therefore increase.

IV. CONCLUSIONS

In this work, we have reported a detailed QCT study of the $\text{C}(^3\text{P}) + \text{OH}(X^2\Pi, v = 0, j) \rightarrow \text{CO}(a^3\Pi, v', j') + \text{H}(^2\text{S})$ reaction on the $1^2\text{A}''$ first excited PES. Excitation function has been calculated up to 0.7 eV. Product rotational and vibrational distributions and DCSs have been shown at four E_c , 0.01, 0.05, 0.1 and 0.5 eV and comparisons with the

results from a SQM approach have been established to understand the precise dynamical mechanisms which govern the reaction. The vibrational distribution is found non-inverted and the rotational distributions are bell-shaped. The DCSs are nearly symmetric and present pronounced forward and backward peaks, which are also observed in the vibrationally state-resolved DCSs. These features are well reproduced in general by the statistical predictions thus supporting the possibility of a complex-forming reaction dominated by an indirect mechanism. This behaviour seems to extend for a broad range of energy since product distributions are similar for all considered collision energies. This is in contrast with the C + OH reaction on the ground state PES which proceeds via a direct process, involving a very short-lived intermediate complex. The findings have to be confirmed by a state-to-state accurate quantum dynamics study (including all partial waves J) and experiments on the C + OH system.

Finally, we plan to study the C + OH reaction dynamics by considering the non-adiabatic couplings between the different PESs computed in a previous work [9], especially the X²A'-1²A" Renner-Teller coupling.

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FIGURES CAPTIONS

FIGURE 1. Schematic energy profile for the $\text{C} + \text{OH} \rightarrow \text{CO} + \text{H}$ reaction on the ground and first excited state PESs.

FIGURE 2. QCT reaction probability, $\langle P_r \rangle = N_r/N_{tot}$, (in black) for all values of the impact parameter b , in terms of the collision energy. Contributions coming from trajectories exploring the HCO potential well (in blue), the COH potential well (in green) and both potential wells (in red) are shown separately.

FIGURE 3. QCT, SQM and TIQM total reaction probabilities at $J = 0$ as a function of the collision energy for the $\text{C} + \text{OH} \rightarrow \text{CO} + \text{H}$ reaction.

FIGURE 4. QCT integral cross sections (in $\text{\AA}^2$) as a function of the collision energy for the $\text{C} + \text{OH}(v = 0, j = 0, 1, 5) \rightarrow \text{CO}(\text{a}^3\Pi) + \text{H}$ reaction. SQM results for $\text{OH}(v = 0, j = 0)$ (in inverted full triangles) have been added for comparison.

FIGURE 5. Product vibrational distributions. Integral cross sections (in $\text{\AA}^2$) at 0.01, 0.05, 0.1 and 0.5 eV for the $\text{C} + \text{OH}(v = 0, j = 0) \rightarrow \text{CO}(\text{a}^3\Pi, v') + \text{H}$ reaction. QCT results are in solid symbols and SQM values are in empty symbols.

FIGURE 6. QCT (solid lines) and SQM (dashed lines) integral cross sections (in $\text{\AA}^2$) at 0.01, 0.05, 0.1 and 0.5 eV for the $\text{C} + \text{OH}(v = 0, j = 0) \rightarrow \text{CO}(\text{a}^3\Pi, v', j') + \text{H}$ reaction.

FIGURE 7. QCT and SQM total differential cross sections (in $\text{\AA}^2/\text{sr}$) at 0.01, 0.05, 0.1 and 0.5 eV for the $\text{C} + \text{OH}(v = 0, j = 0) \rightarrow \text{CO}(\text{a}^3\Pi) + \text{H}$ reaction.

FIGURE 8. QCT and SQM vibrationally state-resolved differential cross sections (in $\text{\AA}^2/\text{sr}$) at 0.01, 0.05, 0.1 and 0.5 eV for the $\text{C} + \text{OH}(v = 0, j = 0) \rightarrow \text{CO}(\text{a}^3\Pi, v') + \text{H}$ reaction.

FIGURE 9. Dependence on the collision energy of the average fraction of the total available energy in the product motion for rotation, vibration or translation ($\langle f_r \rangle$, $\langle f_v \rangle$, or $\langle f_t \rangle$) for $\text{C} + \text{OH}(v = 0, j = 0) \rightarrow \text{CO}(\text{a}^3\Pi) + \text{H}$.

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- [1] Daranlot, J.; Jorfi, M.; Xie, C.; Bergeat, A.; Costes, M.; Caubet, P.; Xie, D.; Guo, H.; Honvault, P.; Hickson, K. M. *Science* **2011**, *334*, 1538.
- [2] Zanchet, A.; Halvick, P.; Rayez, J.-C.; Bussery-Honvault, B.; Honvault, P. *J. Chem. Phys.* **2007**, *126*, 184308.
- [3] Zanchet, A.; Bussery-Honvault, B.; Honvault, P. *J. Phys. Chem. A* **2006**, *110*, 12017.
- [4] Zanchet, A.; Halvick, P.; Bussery-Honvault, B.; Honvault, P. *J. Chem. Phys.* **2008**, *128*, 204301.
- [5] Zanchet, A.; Roncero, O.; González-Lezana, T.; Rodríguez-López, A.; Aguado, A.; Sanz-Sanz, C.; Gómez-Carrasco, S. *J. Phys. Chem. A* **2009**, *113*, 14488.
- [6] Lin, S. Y.; Guo, H.; Honvault, P. *Chem. Phys. Lett.* **2008**, *453*, 140.
- [7] Bulut, N.; Zanchet, A.; Honvault, P.; Bussery-Honvault, B.; Bañares, L. *J. Chem. Phys.* **2009**, *130*, 194303.
- [8] Jorfi, M.; Bussery-Honvault, B.; Honvault, P.; Stoecklin, T.; Larrégaray, P.; Halvick, P. *J. Phys. Chem. A* **2010**, *114*, 7494.
- [9] Zanchet, A.; Bussery-Honvault, B.; Jorfi, M.; Honvault, P. *Phys. Chem. Chem. Phys.* **2009**, *11*, 6182.
- [10] Ho, T.-S.; Rabitz, H. *J. Chem. Phys.* **1996**, *104*, 2584.
- [11] Zanchet, A.; González-Lezana, T.; Roncero, O.; Jorfi, M.; Honvault, P.; Hankel, M. *J. Chem. Phys.* **2012**, *136*, 164309.
- [12] Jorfi, M.; Honvault, P. *J. Phys. Chem. A* **2010**, *114*, 4742.
- [13] Halvick, P.; Rayez, J. C. *Chem. Phys.* **1989**, *131*, 375.
- [14] Rackham, E. J.; Huarte-Larrañaga, F.; Manolopoulos, D. E. *Chem. Phys. Lett.* **2001**, *343*, 356.
- [15] Rackham, E. J.; González-Lezana, T.; Manolopoulos, D. E. *J. Chem. Phys.* **2003**, *119*, 12895.
- [16] González-Lezana, T. *Int. Rev. Phys. Chem.* **2007**, *26*, 29.
- [17] Bargueño, P.; Jambrina, P. G.; Alvariño, J. M.; Hernández, M. L.; Aoiz, F. J.; Menéndez, M.; Verdasco, E.; González-Lezana, T. *J. Phys. Chem. A* **2009**, *113*, 14237.
- [18] González-Lezana, T.; Honvault, P.; Jambrina, P. G.; Aoiz, F. J.; Launay, J. M. *J. Chem. Phys.* **2009**, *131*, 044315.

- [19] Jorfi, M.; Honvault, P.; Bargueño, P.; González-Lezana, T.; Larrégaray, P.; Bonnet, L.; Halvick, P. *J. Chem. Phys.* **2009**, *130*.
- [20] Bargueño, P.; Jambrina, P. G.; Alvariño, J. M.; Menéndez, M.; Verdasco, E.; Hankel, M.; Smith, S. C.; Aoiz, F. J.; González-Lezana, T. *Phys. Chem. Chem. Phys.* **2011**, *13*, 8502.
- [21] Bonnet, L.; Larrégaray, P.; Rayez, J. C.; González-Lezana, T. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3951.
- [22] Bonnet, L.; Larrégaray, P.; Rayez, J. C. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3228.