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Study of the H+O₂ reaction by means of quantum mechanical and statistical approaches: The dynamics on two different potential energy surfaces

Pedro Bargaño,^{1,a)} Tomás González-Lezana,^{1,b)} Pascal Larrégaray,^{2,c)} Laurent Bonnet,² Jean-Claude Rayez,² Marlies Hankel,^{3,d)} Sean C. Smith,³ and Anthony J. H. M. Meijer^{4,e)}

¹*Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain*

²*Institut des Sciences Moléculaires, UMR 5255, Université Bordeaux I/CNRS, 351 Cours de la Libération, 33405 Talence Cedex, France*

³*Centre for Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Queensland 4072, Australia*

⁴*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom*

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The possible existence of a complex-forming pathway for the H+O₂ reaction has been investigated by means of both quantum mechanical and statistical techniques. Reaction probabilities, integral cross sections, and differential cross sections have been obtained with a statistical quantum method and the mean potential phase space theory. The statistical predictions are compared to exact results calculated by means of time dependent wave packet methods and a previously reported time independent exact quantum mechanical approach using the double many-body expansion (DMBE IV) potential energy surface (PES) [Pastrana *et al.*, *J. Phys. Chem.* **94**, 8073 (1990)] and the recently developed surface (denoted XXZLG) by Xu *et al.* [*J. Chem. Phys.* **122**, 244305 (2005)]. The statistical approaches are found to reproduce only some of the exact total reaction probabilities for low total angular momenta obtained with the DMBE IV PES and some of the cross sections calculated at energy values close to the reaction threshold for the XXZLG surface. Serious discrepancies with the exact integral cross sections at higher energy put into question the possible statistical nature of the title reaction. However, at a collision energy of 1.6 eV, statistical rotationally resolved cross sections managed to reproduce the experimental cross sections for the H+O₂($v=0, j=1$) \rightarrow OH($v'=1, j'$)+O process reasonably well. © 2008 American Institute of Physics. [DOI: 10.1063/1.2944246]

I. INTRODUCTION

In the last few years a number of studies have been published on the subject of the H+O₂ reaction. A strong incentive for this renewed interest in the dynamics of this process may be the recent development of a new potential energy surface (PES) denoted XXZLG.^{1,2} Since its publication a couple of years ago, this PES has been employed to calculate bound states, reaction probabilities, integral cross sections (ICs), differential cross sections (DCs), and rate constants for both the title reaction^{1,3-7} and the corresponding reverse reactive collision O+OH.^{2,8} The study of several dynamical features has revealed some striking differences between this new XXZLG surface and the extensively used DMBE IV PES.⁹ Thus, for instance, a better agreement with experimental band origins is obtained with the vibrational frequencies calculated on the XXZLG PES in comparison with previous results on the DMBE IV surface. In addition, reaction probabilities calculated on both PESs exhibit notice-

able distinct profiles and a shift of about 0.1 eV between the corresponding thresholds to reaction.^{3,7} Estimations of the rate constant for the O+OH reaction on the XXZLG and DMBE IV surfaces on the contrary were found to be very similar.²

One of the most discussed issues regarding the H+O₂ process is the possibility of a complex-forming mechanism as the main reaction pathway and the subsequent description of the collision dynamics by means of statistical methods.^{10,11} The topology of the PES, with a deep potential well of about 2.378 eV and the absence of any barrier in the entrance channel, invites to conceive the idea of a strongly bound HO₂ radical as an intermediate between reactants and products. Thus, it should not be surprising to find a long list of kinetical studies in which thermal constants for the title reaction and its reverse have been calculated by means of statistical rate theories (see, for example, Refs. 12–17). In fact, it has been suggested that the dynamical scenario for the process consists of a long-lived complex governing the reaction at low energy in coexistence with a direct reaction mechanism at high energy.¹⁸⁻²¹ In particular, a recent time dependent wave packet (TDWP) calculation on the DMBE IV PES (Ref. 22) concluded that the existence of many narrow resonances (specially visible for low values of the total angular momentum, J) below 1.15 eV collision energy E_c

^{a)}Permanent address: Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain.

^{b)}Electronic mail: tglezana@imaff.cfmac.csic.es.

^{c)}Electronic mail: p.larreagaray@ism.u-bordeaux1.fr.

^{d)}Electronic mail: m.hankel@uq.edu.au.

^{e)}Electronic mail: a.meijer@sheffield.ac.uk.

could be interpreted as an indication of the formation of an intermediate complex at that energy regime. The much broader peaks in the reaction probability at $E_c > 1.15$ eV were attributed to a direct pathway. Further support for these conjectures was obtained with the results of the application of a statistical quantum method^{23,24} (SQM) and a phase space theory (PST) approach²⁵ to investigate the dynamics of the title reaction employing the DMBE IV PES.¹¹ In that study the statistical approaches were found to yield an average description of the $J=0$ exact reaction probability at the low energy range up to 1.15 eV. Beyond that energy, the sudden increase in the reactivity exhibited by the TDWP probability^{22,26,27} cannot be reproduced statistically. Moreover, the comparison with state-to-state exact quantum mechanical (EQM) results²⁸ revealed that the main reason for such deviations from a statistical behavior was the marked preference for the formation of $\text{OH}(v'=0, j')$ fragments in highly excited rotational states, $j' > 13$. This partially statistical behavior of the dynamics on the DMBE IV PES was also observed in the study by Lin *et al.*²⁹ Based on the long lifetime of the intermediate complex and the fact that the $\text{H}+\text{O}_2$ reaction seems to be dominated by long-lived resonances, a wave packet version of the SQM of Ref. 23 was employed to compute the rate constant of the title $\text{H}+\text{O}_2$ reaction, its reverse $\text{O}+\text{OH}$ reaction, and the capture rate of the $\text{H}+\text{O}_2 \rightarrow \text{HO}_2$ process. The agreement found with experimental results was considered as excellent by the authors. In addition, studies of the unimolecular dissociation of the HO_2 complex into the $\text{H}+\text{O}_2$ fragments using the DMBE IV PES revealed significant statistical properties concerning the HO_2 species: The Ramsperger–Rice–Kassel–Marcus dissociation rates were found to agree quite well with the average value of the fluctuating EQM results.^{30–32} Moreover, the vibrotational O_2 distributions could be described through statistical-based methods,^{33,34} in particular, within the framework of the statistico-dynamical approach.³⁵

Despite the above mentioned reports in support of a dominant complex-forming mechanism for the $\text{H}+\text{O}_2$ reaction dynamics as described by the DMBE IV PES, the question is far from settled. Previous trajectory calculations^{9,36} and transition state theory studies³⁷ on this surface have detected significant nonstatistical features attributed to recrossing effects. Similar deviations from a complete statistical behavior have been also reported^{38,39} for the surface by Melius and Blint⁴⁰ and for the global PES by Troe and co-workers.^{14,39,41} Furthermore, although statistical predictions reported in the study by Bargueño *et al.*¹¹ were certainly close to measured cross sections, most of the achievements to give account for some dynamical aspects of the $\text{H}+\text{O}_2$ reaction regarded only to the reactivity at either zero or low total angular momentum J . The statistical total cross section, for instance, clearly overestimates the EQM result. In this sense, the differences observed in the $J=0$ reaction probabilities obtained with the XXZLG and DMBE IV PESs suggest that perhaps the former surface is even more favorable for a complex-forming reaction than the latter. In particular, previously reported probabilities clearly show that the increase beyond $E_c=1.15$ eV, identified as the origin of the deviations from a statistical behavior, does not exist on

the XXZLG PES.^{3,7} This expectation is nevertheless at odds with preliminary evidences of nonstatistical features of the reaction. In particular, the analyses of the bound state levels and low-lying resonances of the HO_2 system for $J=0$ (Ref. 4) indicate significant regularity in the vibrational spectrum, in contrast with the irregularity observed on the DMBE IV PES,^{42–44} which would be consistent with the energy randomization process assumed in the statistical analysis of the corresponding bimolecular process. DCSs calculated on the XXZLG PES near the reaction threshold, on the other hand, exhibit some asymmetry in the forward and backward scattering peaks. This feature was interpreted by the authors of Ref. 6 as indications of relatively short-lived resonances.

In this work, we employ two different statistical approaches to investigate the issue of possible insertion dynamics for the $\text{H}+\text{O}_2$ reaction on the above two mentioned PESs. First, we consider the SQM of Refs. 23 and 24. In accordance with previous studies which indicate that helicity decoupling frameworks introduce inaccuracies, specially when the $\text{H}+\text{O}_2$ arrangement is studied,^{5,29,45–49} the model has been used in its coupled-channel (CC) version with no Coriolis coupling approximation. Comparisons with results obtained within the centrifugal-sudden (CS) approximation^{50–52} will allow to expose the discrepancies generated by such an approach. It is worth mentioning that the present study on the effect of the Coriolis coupling terms is limited to the asymptotic regions considered in the framework of the SQM. The consistency with previous conclusions from the exact calculations will be though investigated. In this sense, for other reactions, the use of the CS version of the statistical model has been found to introduce some inaccuracies on state-to-state resolved magnitudes.⁵³ To the best of our knowledge, this is the first time that a statistical approach is employed for the XXZLG PES. Second, we apply the recently proposed mean potential PST (MPPST).⁵⁴ The method consists in a nonconventional application of PST to effectively account for anisotropies in the asymptotic reactant and product channels.

The present analysis of the $\text{H}+\text{O}_2$ reaction involves the study of reaction probabilities, ICSs, and DCSs. Statistical predictions of such quantities are compared to the corresponding exact results. In particular, exact TDWP reaction probabilities for various values of the total angular momentum J (Refs. 7, 11, 22, 46, and 47) and ICSs (Refs. 11, 55, and 56) have been previously reported for the DMBE IV PES. Analogously, for the XXZLG PES, there exist a vast number of studies which have reported reaction probabilities^{3,5,7} and ICSs.^{5,6} Furthermore, Honvault *et al.*⁶ have recently used the XXZLG PES to obtain DCSs for energies close to the reaction threshold by means of a time independent (TI) EQM approach. In some cases, as explained below, we have extended some of the calculations presented in Ref. 7.

This paper constitutes a comparative study in many ways. First, we propose an analysis of the dynamics of the $\text{H}+\text{O}_2$ reaction using EQM, SQM, and MPPST methodologies and employing two different PESs: the DMBE IV and the XXZLG surfaces, respectively. The statistical predictions are compared to EQM results, with reaction probabilities and

ICSs obtained with the TDWP approaches of Refs. 5, 7, and 11 and the DCSs reported in the TI EQM calculation of Ref. 6. In addition, possible differences between the results obtained by means of the two statistical methods employed here, the SQM and MPPST, are investigated. The issue of the poor performance of the CS approximation for the title reaction is tested by comparing to the CC version of the SQM.

The paper is structured as follows: In Sec. II, the main theoretical aspects of the TDWP approaches and the two statistical methods employed here, the SQM and MPPST, respectively, are presented. In Sec. III we show the results which are discussed in Sec. IV. Finally, in Sec. V, we list the main conclusions of the present study.

II. THEORY

A. Quantum time dependent wave packet calculations

Two different computer programs, TDWP1 and TDWP2, were used in our calculations employing the XXZLG PES. TDWP1 deals with $J=0$ only and uses the real wave packet approach by Gray and Balint-Kurti⁵⁷ in product coordinates to be able to obtain state-to-state reaction probabilities. The TDWP1 program has been employed to obtain all $J=0$ results for the XXZLG surface presented in this paper. In TDWP1 the application of the kinetic energy onto the wave packet is done using discrete variable representation (DVR) based on Gauss–Legendre quadrature points for the angular part, and the radial kinetic energy terms are evaluated using fast Fourier transforms.^{57–59} The analysis is done using the asymptotic matching method by Balint-Kurti *et al.*^{57,60}

TDWP2 deals with $J \geq 0$ and also uses the real wave packet approach, but in reactant coordinates. Moreover, a wrapped sinc-DVR (Ref. 61) is used for the application of the kinetic energy operator. In addition, a point selection scheme is used to speedup the calculations.²² The analysis in TDWP2 is done using a flux analysis method.^{27,62} The TDWP2 method has been employed for the extended $J=2$ and $J=4$ calculations for the XXZLG PES presented in the current paper.

All parameters used in the TDWP1 and TDWP2 calculations are listed in Table I of Ref. 7. In all TDWP1 calculations the wave packet has been propagated for 50 000 steps. In the current TDWP2 calculations presented here the wave packet was propagated for 60 000 steps. This differs from the calculations presented in Ref. 7, where 35 000 steps were deemed to be sufficient. As will be discussed in Sec. III B, longer propagation times were found to be necessary in the current calculations. Both methods employed are well documented in the literature. For more details, see, for example, Refs. 22, 46, 55, and 57–59.

The calculations for the DMBE IV PES have been performed with the TDWP approach described in Refs. 11 and 26. Hereafter we will refer to this method as TDWP3. We suggest the above mentioned references to the interested reader for a proper discussion regarding the theoretical details of this code.

B. Statistical quantum method

The theory on the SQM model has been presented in several occasions before,^{10,23,24} so here we will only discuss the most relevant aspects. The method is conceived to deal with complex-forming atom-diatom reactions. TI log derivative calculations are done separately in each arrangement, restricted to the region which extends from the asymptotic situation with the separated atom-diatom fragments up to certain capture radius where the complex is assumed to exist. The individual capture probabilities p_i^{JJ} at specific values of the total angular momentum J and the QM parity I are thus obtained, and the state-to-state reaction probability is approximated as

$$|S_{v'j'\Omega',vj\Omega}^{JJ}(E)|^2 \approx \frac{P_{v'j'\Omega'}^{JJ}(E)P_{vj\Omega}^{JJ}(E)}{\sum_{v''j''\Omega''} P_{v''j''\Omega''}^{JJ}(E)}. \quad (1)$$

In the above expression, v and j refer to the diatomic vibrational and rotational quantum numbers, respectively, of the reactant O₂ fragment and Ω is the modulus of the projection of the diatomic rotational angular momentum on the atom-diatom axis. The corresponding values of those quantum numbers for the product OH diatom are expressed with primes. In Eq. (1), the sum in the denominator is extended to all energetically open vibrotational states in both reactant and product arrangements.

The statistical state-to-state ICS is then evaluated from the corresponding QM expression,

$$\sigma_{v'j',vj}(E) = \frac{\pi}{gk_{vj}^2(2j+1)} \sum_{I\Omega\Omega'} (2J+1) |S_{v'j'\Omega',vj\Omega}^{JJ}(E)|^2, \quad (2)$$

with $k_{vj}^2 = 2\mu(E - E_{vj})/h^2$, E_{vj} being the energy of the initial rovibrational state vj of the reactant diatom, μ the atom-diatom reduced mass, and g the electronic degeneracy, which in the case of H+O₂ is 3. For the reactive probability $|S_{v'j'\Omega',vj\Omega}^{JJ}(E)|^2$ we consider the statistical approximation of Eq. (1).

Since the SQM approach only enables the computation of the square modulus of the scattering matrix, the calculation of DCSs requires the use of a further approximation. Thus, under the random phase assumption,²⁴ the expression of the DCS is the following:

$$\sigma_{v'j',vj}(\theta, E) \approx \frac{1}{8k_{vj}^2} \frac{1}{2j+1} \sum_{I\Omega\Omega'} (2J+1)^2 [d_{\Omega'\Omega}^J(\pi - \theta)^2 + d_{\Omega'\Omega}^J(\theta)^2] |S_{v'j'\Omega',vj\Omega}^{JJ}(E)|^2, \quad (3)$$

where $d_{\Omega'\Omega}^J$ is a reduced rotation matrix element.

As indicated in the Introduction all calculations were performed within the CC version. Hereafter we will only refer to this “exact” statistical version as SQM-CC when we compare to the results obtained within the CS approximation (SQM-CS). On all other occurrences this method is referred to as SQM. We note by passing that even with the considerable reduction in the computation time introduced with the SQM compared to an EQM method, the calculation of ICSs

with the CC code at the larger values of the energy shown here can be prohibitive. The numerical difficulty is found mainly in the reactant channel $\text{H}+\text{O}_2$, where the number of $\text{O}_2(v, j)$ vibrotational states is extremely large as compared to the corresponding $\text{OH}(v', j')$ product states. In order to obtain total and state-to-state cross sections at 1.6 eV collision energy, for large values of the total angular momentum J , it was necessary to limit the number of rotational states j included in the SQM-CC calculation in the reactant channel. The largest value of j required for the calculation at $E_c = 1.6$ eV was $j \sim 87$, corresponding to the ground O_2 vibrational state. Statistical calculations considering different $[j = 1, j_{\max}^{(0)}], [j_{\max}^{(0)} + 2, j_{\max}^{(1)}], \dots, [j_{\max}^{(n-1)} + 2, j_{\max}^{(n)}], [j_{\max}^{(n)} + 2, j = 87]$ sequences were carried out to achieve converged results. Tests of such a procedure at lower energy values yielded no differences with the corresponding calculation with no restrictions on the number of rotational states. Capture probabilities $p_{vj\Omega}^J$ for all the accessible reactant diatom states were thus constructed by addition of the outputs from those separate calculations. Furthermore the SQM-CC calculation was only carried out for even values of J up to $J=80$. State-to-state probabilities for $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{OH}(v', j') + \text{O}$ at $E_c = 1.6$ eV were obtained for those calculated J . The corresponding values at J odd values were estimated by interpolation of these opacity functions.

C. Mean potential phase space theory

The MPPST consists of an unusual implementation of PST which approximately accounts for anisotropies in the asymptotic channels.⁵⁴ To that end, instead of approximating the potential energies of interaction between separated fragments by their isotropic long-range contributions, usually estimated from the Slater–Kirkwood model in PST, the latter are replaced by the accurate potential energies averaged with respect to Jacobi angles over attractive regions. As in the original PST, a microcanonical distribution of the phase space states of the intermediate long-lived complex is assumed.²⁵ Consequently, ICSs and DCSs are shown to be completely determined by capture fluxes in the entrance and exit channels,⁶³ which can be computed through phase space integrals. The approach is semiclassical in that the diatom vibration motions are quantized, whereas the rotation/translation motions are treated classically. MPPST has been shown to lead to results in very satisfying agreement with the predictions of the TI and time dependent quantum statistical models for the $A+\text{H}_2$ reactions with $A=C(^1D)$ and $S(^1D)$.⁵⁴ Technical details for implementation of such a model are presented in Refs. 54, 64, and 65.

III. RESULTS

As mentioned in previous sections, this study focuses on the analyses of reaction probabilities, ICSs, and DCSs. In particular, we separate the case of a zero total angular momentum and those situations in which $J > 0$. Particular emphasis is placed on the comparison between the observed dynamics on both PESs.

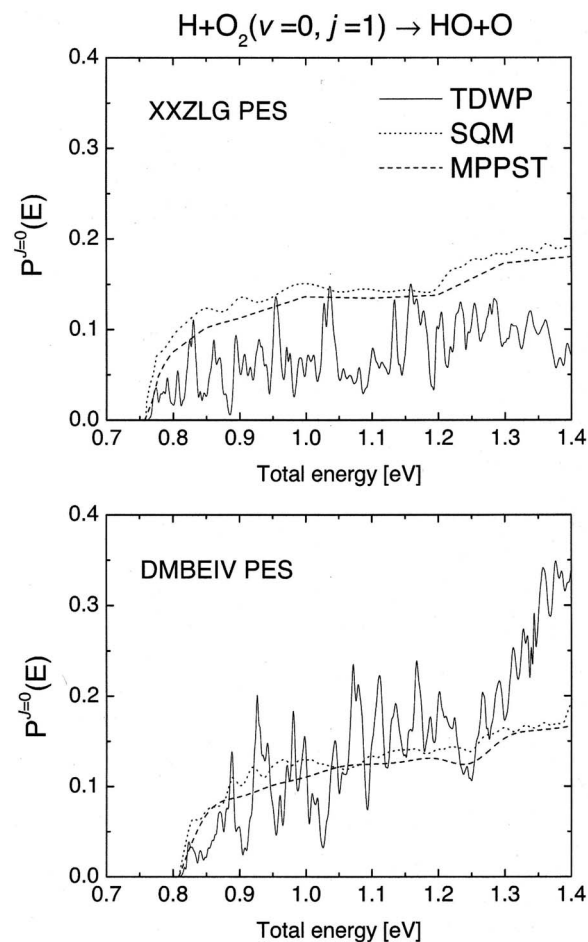


FIG. 1. Total reaction probabilities in terms of the total energy for $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{HO}+\text{O}$ on the XXZLG (top panel) and DMBE IV (bottom panel) PESs obtained by means of the TDWP1 (Ref. 7) and TDWP3 (Ref. 11) (in solid line), respectively, the SQM (dotted line) and the MPPST (dashed line) approaches for zero total angular momentum.

A. $J=0$ reaction probabilities

The total reaction probabilities for the $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{OH}+\text{O}$ reaction at zero total angular momentum employing the DMBE IV and XXZLG PESs are given in Fig. 1. The corresponding EQM results have been taken from previously reported calculations by means of the TDWP3 (Ref. 11) and TDWP1 (Ref. 7) codes, respectively. A similar comparison between exact probabilities and the corresponding statistical predictions on the DMBE IV surface has been shown before.¹¹ As indicated there, both statistical approaches yield reaction probabilities which are in remarkably good accord with the average value of the TDWP result. Such agreement is more noticeable at energies below ~ 1.25 eV total energy; beyond that value, which is close to the onset of the $\text{OH}(v'=1)$ product channel, the exact probability increases. Neither the SQM nor the MPPST outputs seem to follow that sudden increase in the reactivity. The fact that the apparent success of the statistical methods to reproduce the exact result depends on the energy range considered can be interpreted, as suggested before,²² in terms of the existence of two distinct dynamical mechanisms: At the low energy regime, an intermediate complex mediated dynamics would be consistent with a statistical description of the pro-

cess, whereas the deviation of the TDWP probability with respect to any statistical description at higher energy would suggest the onset of a direct reaction mechanism. The MPPST result for the reactivity at $J=0$, on the other hand, does not differ significantly from the previous estimations obtained with the usual PST approach.¹¹

One of the most distinguishable features of the $J=0$ reaction probability for the XXZLG surface in comparison with the DMBE IV PES is the absence of the above mentioned increase at the high energy regime. Since at those energies the discrepancies with the SQM and MPPST results are larger, one might expect an overall better description of the reaction probability by statistical means on the XXZLG surface. The observed situation differs, however, notably from those expectations. The TDWP reaction probability is significantly smaller over the whole energy range under consideration on the XXZLG PES. The obtained statistical $P(J=0, E)$ probability curves, which apart of the shift in the reaction threshold introduced by the different potential surface, hardly vary from those on the DMBE IV PES. The statistical results therefore do not provide the expected average description of the EQM results but overestimate the exact probabilities.

Further insight into the dynamics of the title reaction on the XXZLG PES at zero total angular momentum is gained at the state-to-state level. Exact reaction probabilities for different $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{OH}(v'=0, j')+\text{O}$ processes were calculated by means of the TDWP1 approach. The $j'=0, 7$, and 14 cases are shown in Fig. 2 together with the statistical counterpart provided by the SQM approach. In the study by Hankel *et al.*⁷ energy averaged rotational distributions for $J=0$ were obtained, but as in Ref. 11 we prefer to compare the EQM and SQM state-to-state reaction probabilities not averaged with respect to the collision energy. Such a comparison enabled us to distinguish that the major discrepancies between both approaches have their origin in the propensity of formation of highly excited rotational states of the OH fragment as evidenced by the EQM probabilities.¹¹ This seems not to be the case for the XXZLG PES since reaction probability of the $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{OH}(v'=0, j'=14)+\text{O}$ process is significantly smaller than for the other j' states analyzed here. In addition, the statistical predictions happen to provide a better description of the TDWP result as the product j' excitation increases. The overestimation found for the total reaction probability (see Fig. 1) seems to be originated from the low j' cases, as seen from the probability for the $\text{OH}(v'=0, j'=0)$ production. For the two other values of j' , the SQM probability constitutes a fair average of the exact result provided by the TDWP calculation.

B. Reaction probabilities for $J>0$

After discussing the $J=0$ reaction probabilities in the previous subsection, we will now analyze the corresponding probabilities for $J>0$. Thus we calculate the total reaction probabilities for the $\text{H}+\text{O}_2(v=0, j=1)$ at $J=2$ and 4 by means of the two statistical approaches employed here, the SQM and the MPPST methods. The results of such calculations are shown in Fig. 3 besides the reaction probabilities

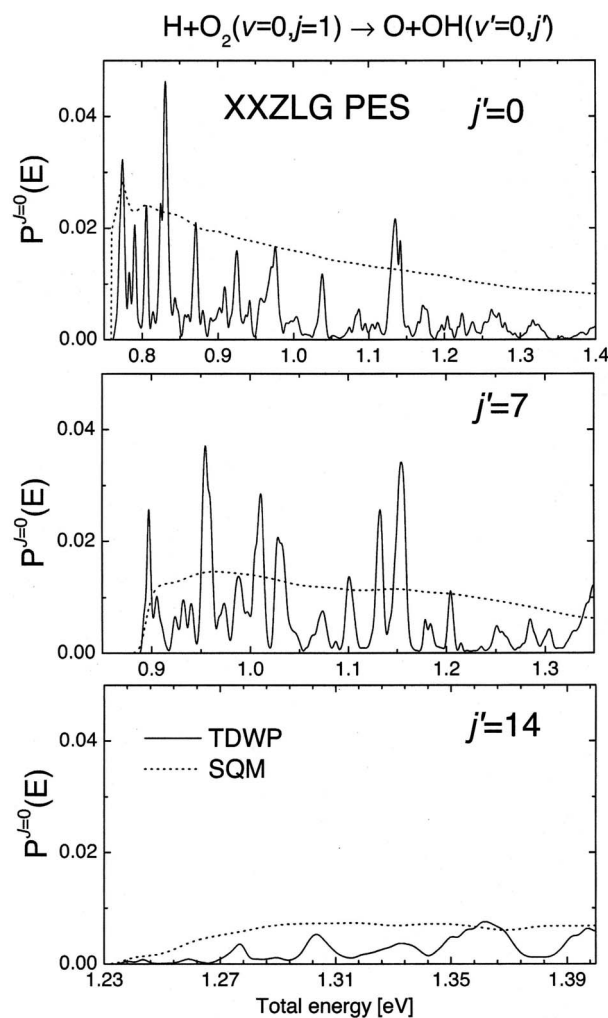


FIG. 2. State-to-state selected probabilities for the $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{OH}(v'=0, j')+\text{O}$ reaction on the XXZLG PES for $j'=0$ (top panel), $j'=7$ (middle panel), and $j'=14$ (bottom panel) at $J=0$. TDWP results, calculated employing TDWP1, are in solid line, and SQM probabilities are in dotted line.

obtained with the TDWP2 calculation. It should be noted here that these probabilities are not exactly the same as those reported in Ref. 7. The reason is that the preliminary comparison with the statistical predictions revealed an unusually large deviation between the corresponding reaction thresholds visible in the figures. In order to test the origin of this discrepancy, calculations performed in the study by Hankel *et al.* were repeated with a longer propagation time. Short times in the propagation correspond to high energy components of the total probability. While the actual reaction threshold should not change, the magnitude at low energy will increase if longer propagation times are included. As a result, some shift in those thresholds was observed, although as Fig. 3 reveals, the statistical results indicate a somewhat earlier reactivity than that exhibited by the TDWP probability. But clearly the most significant conclusion to be drawn from Fig. 3 is that both the SQM and MPPST results are significantly larger than the EQM result. From the two statistical methods, the SQM approach produces probabilities even higher than those obtained by means of the MPPST method. Previous studies^{10,11} carried out on the DMBE IV

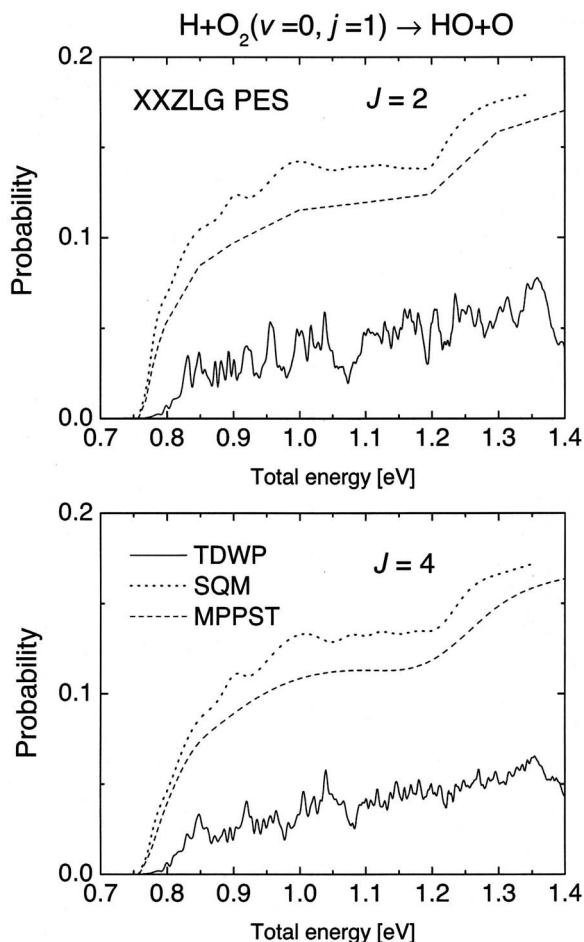


FIG. 3. Total reaction probabilities for the $\text{H}+\text{O}_2(v=0, j=1)$ process at $J=2$ (top panel) and $J=4$ (bottom panel) on the XXZLG PES. TDWP results, calculated employing TDWP2, are in solid line, SQM probabilities in dotted line, and MPPST predictions in dashed line.

PES revealed, on the contrary, that statistical reaction probabilities for low and intermediate values of the total angular momentum ($J < 15$) were not in such evident disagreement with respect to the exact TDWP results as found for the XXZLG PES. In particular, the PST probabilities reported in Ref. 11 were found to be in a fairly good agreement with the EQM values. To investigate this further we have calculated statistical predictions by means of the SQM-CC and MPPST methods for $J=2, 5$, and 15 . The comparison with the TDWP3 reaction probabilities of Ref. 11 is shown in Fig. 4. As mentioned above, both approaches, especially the MPPST, are capable to reproduce the exact results. Despite the fact that the agreement begins to deteriorate as J increases, it is clear that the overall performance of the statistical techniques to describe the dynamics of the collision at this low J regime is very different for both PESs.

Figure 4 also includes the SQM-CS results, that is, those obtained by means of the SQM within the CS approximation. According to the present SQM predictions, this approximation seems not to introduce significant differences with respect to the CC calculations; at least in the range of low-medium values of the total angular momentum considered, $J < 15$. As we will see below, this is not the case when the total angular momentum is increased to even larger values.

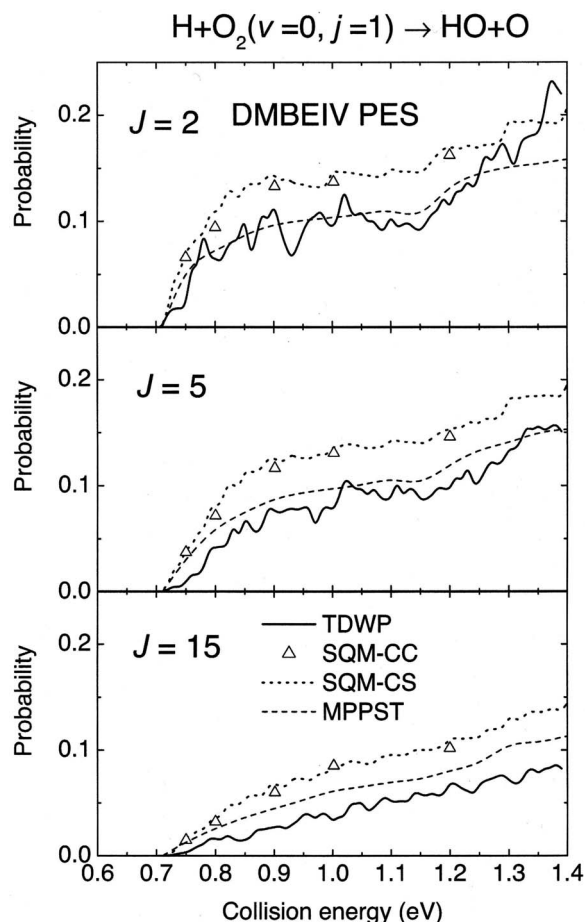


FIG. 4. $J=2$ (top panel), $J=5$ (middle panel), and $J=15$ (bottom panel) reaction probabilities for the $\text{H}+\text{O}_2(v=0, j=1)$ reaction on the DMBE IV PES. TDWP3 and SQM-CS (obtained within the CS approximation), in solid and dotted line, respectively, are from Ref. 11. MPPST predictions are in dashed line, and those obtained by means of the CC version of the SQM calculation are shown with open triangles.

The comparison between the statistical approaches reveals that the MPPST predictions are certainly closer to the TDWP reaction probabilities than those obtained with the SQM. A slight deviation from the exact results as J increases is observed.

These particular dynamical aspects, the comparison between the CS and CC calculations on one hand and the comparison between the statistical approaches and the TDWP reaction probabilities, on the other hand, when the total angular momentum varies, can be further analyzed by calculating the opacity functions. Thus, MPPST and SQM calculations were carried out to obtain the total reaction probabilities of the $\text{H}+\text{O}_2(v=0, j=1) \rightarrow \text{OH}+\text{O}$ process at specific values of the collision energy in terms of J for the two PESs considered in this study. In particular, the opacity functions at $E_c=0.9$ and 0.8 eV for the DMBE IV and XXZLG PESs, respectively, were computed with these statistical approaches. Results of such calculations are shown in Fig. 5 in comparison with EQM probabilities. The TDWP opacity for the DMBE IV surface was obtained from Ref. 11 (see Fig. 5). The corresponding reaction probability for the XXZLG PES has been adapted from the cross sections reported in Ref. 5. It is obvious from the comparison between the

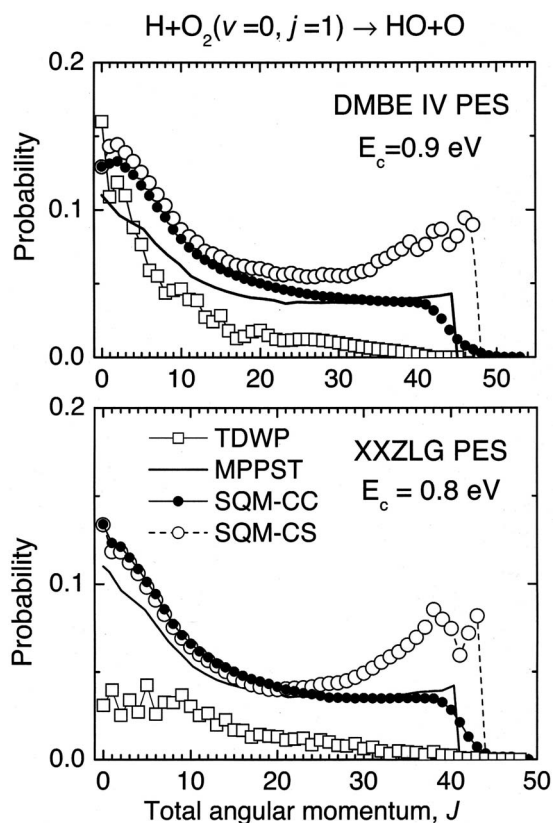


FIG. 5. Initial state resolved probability with respect to the total angular momentum J at 0.9 eV collision energy on the DMBE IV PES (top panel) and at $E_c=0.8$ eV on the XXZLG PES (bottom panel). TDWP results (squares with solid lines) are from Ref. 11, where the TDWP3 code was employed, in top panel and adapted from ICSs of Ref. 5. MPPST probabilities are in solid line, SQM-CS are shown in full circles and solid lines, and SQM-CS results are in open circles and dashed lines.

exact reaction probabilities and those obtained by statistical means shown in Fig. 5 that the overall quality of the statistical predictions for the DMBE IV PES seems to deteriorate as J increases. Both MPPST and SQM results are above the exact probabilities for nearly the whole range of the total angular momentum covered at 0.9 collision energy, but the differences at large values of J ($J \gtrsim 15$) are especially significant. For the XXZLG surface the situation is even more unfavorable for a statistical description of the exact probabilities, since the disagreement between both kinds of results is noticeable even for the lowest values of J . This result is consistent with our observations for a wide range of energy at $J=2$ and 4 (see Fig. 3).

The statistical methods on the other hand give equivalent predictions. Apart from some slight deviations at some specific values of the total angular momentum, the overall accord between the MPPST and the SQM-CC results is certainly remarkable. It is also interesting to point out the substantial differences found at high values of J between the SQM approach in the CC version and under the CS approximation. In particular, the SQM-CS probabilities start to diverge from the SQM-CC result about $J \sim 25$ at both energies and surfaces. Beyond that value of the total angular momentum, the reaction probabilities obtained within the CS approach suddenly increase, deviating from the exact statistical calculation. This finding is entirely consistent with previ-

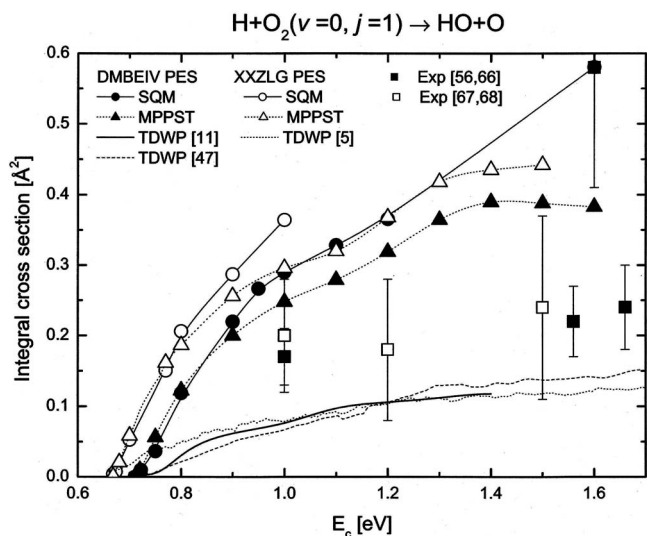


FIG. 6. ICSs measured in \AA^2 obtained on the DMBE IV (full symbols) and the XXZLG PESs (empty symbols) by means of the SQM (solid line and circles), the MPPST (dotted line and triangles), and TDWP approaches from Refs. 11 (solid line), 55 (dashed line), and 5 (dotted line). Experimental results (shown with squares) have been taken from cross sections measurements based on OH (Refs. 67 and 68) and O (Refs. 56 and 66) product detection techniques.

ously published reports of the failure of such an approximation for the H+O₂ reaction in EQM calculations.^{5,29,45–49}

These results illustrate the deficiencies of the CS approach in the framework of statistical techniques, establishing the origin of the discrepancies with the CC method at relatively large values of the total angular momentum.

C. Integral cross sections

Another dynamical feature analyzed in the present study is the ICS for the H+O₂($v=0, j=1$) reaction. In a similar way as for the reaction probabilities discussed above, statistical predictions for the ICSs have been calculated by means of the MPPST and SQM-CC approaches for both the DMBE IV and XXZLG PESs. In Fig. 6 we show such results in the range up to 1.5 eV collision energy. The comparison with exact TDWP cross sections has been included in the figure. The EQM ICSs on the DMBE IV PES correspond to those reported in Refs. 11 (obtained with the TDWP3 approach) and 55 (obtained with the TDWP2 approach). The EQM ICS on the XXZLG PES is the one calculated by Lin *et al.*⁵ A previous comparison (see Fig. 4 of Ref. 5) already revealed that, besides a shift in the corresponding reaction threshold, no significant differences are observed between the exact ICSs obtained on the two surfaces. This feature has been interpreted as an indication of the dominance on the overall reactivity of the product OH+O channel, which is described in a similar way in both the XXZLG and DMBE IV PESs.⁵ Statistical cross sections calculated for each PES exhibit similar behavior with energy, confirming thus that the description of the long range region given in both PESs does not differ substantially in the two cases.

Figure 6 reveals that the statistical approaches do not give a correct estimate of the exact cross sections. Although the thresholds for each potential surface are correctly de-

TABLE I. ICSs, in \AA^2 , for the $\text{H}+\text{O}_2(v,j=1)\rightarrow\text{O}+\text{OH}$ reaction at $E_{\text{tot}}=0.7661$ eV calculated on the XXZLG PES. The TI EQM results reported in Ref. 6 are compared to the SQM and MPPST predictions.

v	TI EQM	SQM	MPPST
0	0.0024	0.0041	0.0010
1	0.0034	0.0055	0.0013
2	0.0069	0.0087	0.0022
3	0.0121	0.0162	0.0058

scribed, neither the MPPST nor the SQM cross sections seem to have the same dependence on energy compared to the TDWP results. The statistical predictions largely overestimate the exact ICSs. It seems then that the observed accord between the statistical and TDWP reaction probabilities at low values of J for the DMBE IV PES is not sufficient to guarantee a correct description of the ICSs. On the contrary, the above discussed deviations from the EQM probabilities at high values of J , with a major contribution in the expression for the cross section due to the $(2J+1)$ weighting factor [see Eq. (2)], preclude the ICSs to exhibit a completely statistical behavior. In addition cross sections obtained with these two statistical methods start to differ about 0.9 collision energy. Both results are almost identical at the low energy regime, but beyond that energy the ICSs computed by means of the SQM are consistently larger than those obtained in the MPPST calculation. The small differences between the MPPST and SQM ICSs at 0.9 and 0.8 eV for the DMBE IV and MPPST PESs, respectively, are therefore consistent with the overall agreement found for the corresponding opacity functions shown in Fig. 5.

In a recent study, Honvault *et al.*⁶ calculated initial state-selected ICSs at a very low total energy, $E_{\text{tot}}=0.7661$ eV, for a series of initial $\text{O}_2(v,j)$ states. The observed trends upon increases in either the vibrational v or rotational quantum number j were considered to be inconsistent with the expected results of a statistical model. In this work, we have employed the MPPST and SQM approaches to test this conclusion. In particular, in Table I, ICSs for the $\text{H}+\text{O}_2(v,j=1)$ reactions for various values of v at $E_{\text{tot}}=0.7661$ eV, from both statistical methods are listed in comparison with the exact cross sections reported in Ref. 6. Neither of the statistical predictions are far from the exact results, and with the only exception of an observed slight deviation of the MPPST values, one could conclude that, at least for this low energy, the two above mentioned methods produce fairly good estimates for the reaction ICSs. It is worth mentioning that the SQM predictions are higher than the EQM ICSs in all cases considered in Table I, whereas the MPPST cross sections remain below.

Figure 6 also shows the comparison between theory and experimental results obtained by means of both O (Refs. 56 and 66) and OH detection techniques.^{67,68} Previous comparisons have revealed that the calculated exact ICSs were clearly lower than the reported measurements, and only in two cases, 1.2 and 1.5 eV collision energies, the theoretical values appear to be within the experimental uncertainty. Exact TDWP approaches are therefore in clear disagreement

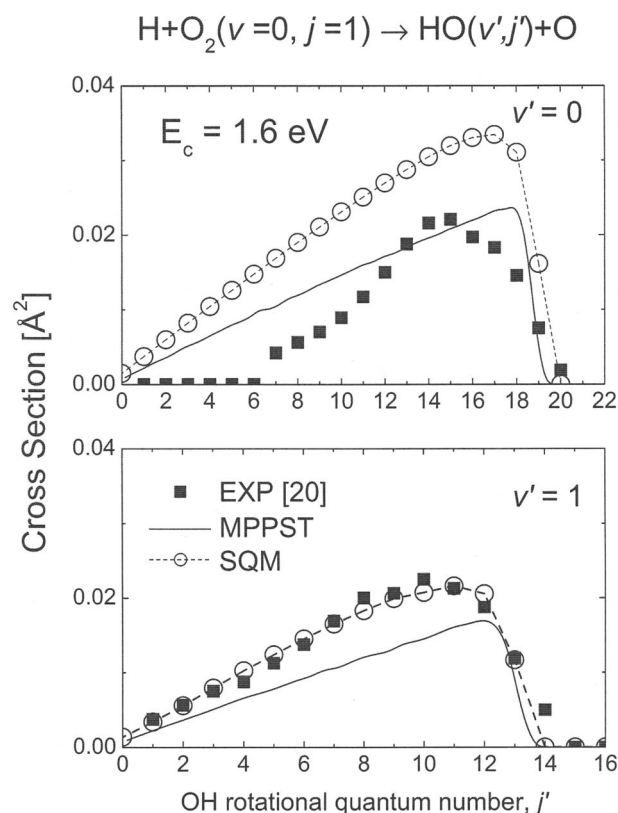


FIG. 7. Rotationally resolved ICSs for the $\text{H}+\text{O}_2(v=0,j=1)\rightarrow\text{OH}(v',j')+\text{O}$ reaction at 1.6 eV collision energy. Cross sections for the production of $\text{OH}(v'=0,j')$ are in top panel and those for the $\text{OH}(v'=1,j')$ are shown in bottom panel. Theoretical results have been obtained with the DMBE IV PES by means of the SQM (empty circles and dashed line) and MPPST (solid line) approaches. Measured cross sections correspond to results reported from Bronikowski *et al.* (Ref. 20) and have been scaled, in both $\text{OH}(v')$ cases, in order to match the SQM prediction for the $\text{OH}(v'=1, j'=7)$ ICS.

with the experimental data. The statistical predictions on the other hand happen to be slightly above the upper limits of the error bars and, with the only exception of $E_c=1.6$ eV, do not agree either with the experimental ICSs. For that particular collision energy, experimental state-to-state resolved ICSs have been reported.²⁰ Previous studies have found that the shape of the rotational distributions for the $\text{OH}(v'=1)$ production channel can be perfectly reproduced by means of statistical results.^{10,11} We have employed both the MPPST approach and the CC version of the SQM with the DMBE IV PES at 1.6 eV collision energy. The result of the comparison of these statistical cross sections to the measured values is shown in Fig. 7. In consistency with the previously reported results of Refs. 10 and 11, the observed population of the $\text{OH}(v'=1, j')$ product states is in agreement with the prediction obtained with the SQM, but the calculated rotationally resolved ICSs for the $\text{H}+\text{O}_2(v=0,j=1)\rightarrow\text{OH}(v'=0,j')+\text{O}$ reaction do not reproduce the experimental results. The present theoretical ICSs differ notably from those reported in Fig. 40 of Ref. 10. In that case, the SQM results were obtained within the CS approximation, which is found to overestimate reaction probabilities for large values of the total angular momentum in comparison with the CC version (see Fig. 5). As a result, the present SQM rotationally resolved

TABLE II. ICSs measured in Å² calculated with the DMBE IV PES at collision energies (in first column in eV), near to the reaction threshold for H+O₂(*v*=0, *j*=1) → OH+O. Statistical predictions obtained with the SQM (in second column) and MPPST (third column) are compared to EQM results from Refs. 11 and 55 (in fourth and fifth columns, respectively). QCT cross sections obtained by means of different variants to overcome ZPE effects from Ref. 19 are included in the last three columns. See text for details.

<i>E_c</i>	Statistical		EQM		QCT ^a		
	SQM	MPPST	Ref. 11	Ref. 55	QMT	IEQMT	VEQMT
0.674	0	0	0	0	0.016 (0.002) ^b		
0.725	0.013	0.018	0.002	0.003		0.019 (0.003)	
0.829	0.145	0.151	0.044	0.030	0.092 (0.008)	0.069 (0.007)	0.018 (0.004)
0.933	0.249	0.218	0.067	0.057			0.045 (0.006)
1.2	0.365	0.320	0.106	0.106		0.163 (0.011)	0.100 (0.008)

^aReference 19.

^bThe usual QCT approach, which is found to agree with the QCT-QMT approach for energies above *E_c* ~ 0.71 eV, predicts a value of the ICS at *E_c* = 0.674 eV of 0.055 ± 0.004 Å².

ICSs are much smaller than those obtained when the Coriolis couplings are neglected. The differences of the present MPPST results and the ICSs obtained with the usual PST approach (see Fig. 7 of Ref. 11) consist mainly on a distinct population of the OH(*v*'=1, *j*' > 9) product rotational states. The disagreement between these MPPST ICSs and the experimental values for the lower OH(*v*'=1, *j*' < 9) states is only due to the fact that the measured distributions have been scaled to match the SQM prediction for OH(*v*'=1, *j*'=7). The different behavior of the MPPST rotational distributions with respect to both the experimental and the SQM values is nevertheless evident for the highest product states. The excess of cross sections for both OH(*v*') product channels predicted by the SQM approach with respect to the other statistical method, the MPPST, explains the difference observed in Fig. 6 for the total ICS at *E_c* = 1.6 eV.

The possible effect of the zero-point energy (ZPE) on the results obtained by means of quasiclassical trajectory (QCT) calculations on the H+O₂ ↔ OH+O reaction is a widely debated issue.^{19,36,39,69,70} In particular, excitation functions have been calculated on the DMBE IV PES by means of QCT approaches which try to solve the ZPE problem in different manners.¹⁹ Among the possible alternatives suggested in Ref. 19, we have compared the statistical predictions for the ICS of the H+O₂(*v*=0, *j*=1) reaction to those obtained with the QCT-quantum mechanical threshold (QCT-QMT), the QCT-internal energy QMT (QCT-IEQMT), and the QCT-vibrational energy QMT (QCT-VEQMT) variants. In the QCT-QMT approach, only those trajectories with enough total energy to reach the ZPE of the products are integrated. This method is found to be identical to the usual QCT method when the collision energy was larger than the difference between the ZPEs of products and reactants (that means *E_c* ~ 0.71 eV for the present reaction). In the QCT-IEQMT and QCT-VEQMT variants, the criterion to accept a trajectory for the corresponding statistical analysis is applied to the internal energy or vibrational energy, respectively, of the final product or the reactant diatomic fragment in case the trajectory turns to be not reactive. In Table II, the values for the ICS at energies close to the reaction threshold reported for the above described three QCT approaches¹⁹ are compared to the statistical (SQM and MPPST) predictions ob-

tained in this work on one hand and with EQM results from previous studies on the other hand.^{11,55} The QCT predictions are, in general, not too far from the exact ICSs. In this sense the comparison with the EQM results reveals that the QCT approaches produce cross sections in an overall better agreement than those ICSs obtained by means of the statistical methods. Values for the QCT-QMT and QCT-IEQMT ICSs are larger, for the energies shown in Table II, than the EQM cross sections, whereas the QCT-VEQMT model yields smaller ICSs than the exact ones. As already discussed above, the SQM and MPPST approaches predict cross sections which overestimate the EQM ICSs. Although the definitive benchmark to elucidate the best strategy to overcome the ZPE problem has to be obviously provided by the EQM results, the good accord in the values of the threshold for reaction found between both QM approaches (statistical and exact) enables either the SQM or MPPST methods to be used in order to get some insight about which one is the most accurate QCT variant discussed here. With the aim to obtain a pictorial description of the behavior with respect to the collision energy of the ICSs calculated with the different theoretical approaches mentioned here, in Fig. 8 we have plotted, for the energy region close to the threshold for reaction (0.6 ≤ *E_c* ≤ 0.9 eV) on the DMBE IV PES the SQM and MPPST predictions for the ICS, those cross sections reported from the EQM calculations of Refs. 11 and 55 and the different QCT results.¹⁹ The statistical functions have been obtained by interpolation of the calculated points, shown in Fig. 6, whereas the corresponding excitation functions for the QCT calculations are the result of a least-squares fit to the same analytical expression considered in the study by Varandas.¹⁹ Although the procedure to obtain the specific function describing the calculated QCT ICSs is not entirely identical to that one reported in Ref. 19, it should suffice for the present discussion.⁷¹ It is clear from Fig. 8 that only the QCT-IEQMT approach seems to yield a threshold for reaction, *E_{thr}*^{IEQMT} ~ 0.7 eV, in certain agreement with the QM value *E_{thr}*^{QM} ~ 0.71 eV. The usual QCT method, however, leads to a far too low energy for such threshold, *E_{thr}*^{QCT} ~ 0.44 eV.¹⁹

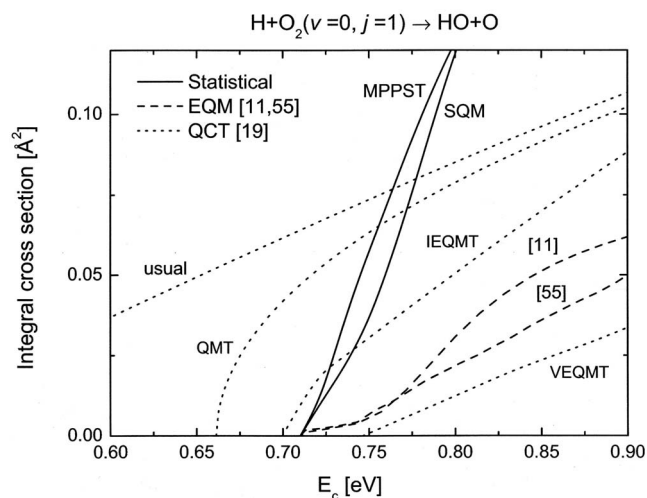


FIG. 8. ICS measured in \AA^2 at collision energies near the threshold for reaction, calculated on the DMBE IV PES by means of the statistical approaches (in solid lines) used in this work (SQM and MPPST), the EQM methods (in dashed lines) from Refs. 11 and 55, and the QCT approaches (in dotted lines) of Ref. 19: the usual QCT method and the QCT-QMT, QCT-IEQMT, and QCT-VEQMT variants, which employ different strategies to overcome the ZPE effects. The statistical cross section curves have been obtained by interpolating the calculated points up to $E_c=0.9$ eV shown in Fig. 6, and the ICS functions of the QCT calculations have been extracted from least squares fits to the same analytical form employed in Ref. 19. See text and Ref. 71 for further details.

D. Differential cross sections

Only quite recently have EQM DCSs been reported for the title reaction.⁶ In the context of an investigation regarding the possible occurrence or not of complex-forming reaction mechanisms for the $\text{H}+\text{O}_2$ process, the precise shape of the angular distributions can supply useful information about the dominant dynamics. The comparison of DCSs obtained by means of statistical tools with those recent exact results therefore constitute a quite attractive test to complete the present dynamical study. Thus we have employed the MPPST and SQM-CC approaches to calculate DCSs for some of the initially state-selected processes considered in the EQM study of Ref. 6.

In Fig. 9 we compare the statistical DCSs to the corresponding exact angular cross sections for the $\text{H}+\text{O}_2(v,j=1)\rightarrow\text{OH}+\text{O}$ reactions, with $v=0-3$ at 0.7661 eV total energy on the XXZLG PES.⁷² In their analysis of the DCSs found at that specific energy, the authors of Ref. 6 conceded that the propensity of the TI EQM angular distributions to exhibit pronounced peaks at the forward ($\theta\approx 0^\circ$) and backward ($\theta\approx 180^\circ$) scattering directions could be indicative of the formation of an intermediate complex. In their opinion, the slightly asymmetrical profile precludes a complete statistical origin. The comparison shown in Fig. 9 reveals, however, that, despite the expected discrepancies observed for those cases with a more pronounced asymmetry ($v=1$ and 2), the description provided by the statistical approaches is not bad. Thus, the average description of the TI EQM distributions at the sideways scattering direction ($50^\circ\lesssim\theta\lesssim 130^\circ$) is fairly good and for $v=1$ and 2, the cases in which certain propensity on the forward-backward peaks is observed, the SQM value for the $\theta\approx 0^\circ$ maximum is in good agreement

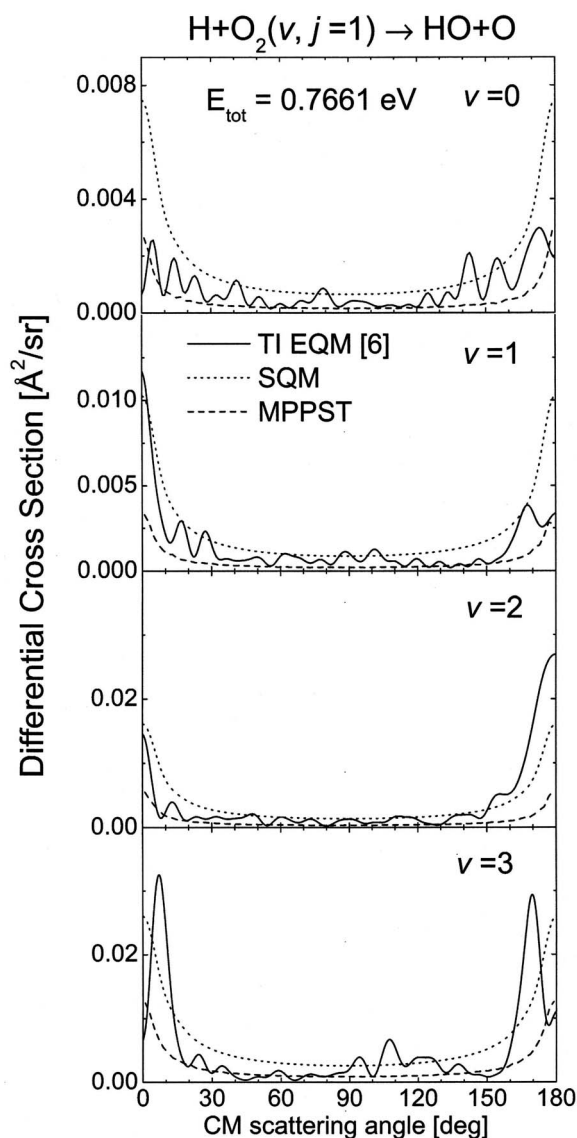


FIG. 9. DCSs calculated on the XXZLG PES at 0.7661 eV total energy for the $\text{H}+\text{O}_2(v,j=1)$ reaction, for $v=0$ to 3 from top to bottom panels. Units are $\text{\AA}^2/\text{sr}$. Exact results (in solid lines), which are TI DCSs from Ref. 6, are compared to the MPPST (dashed line) and SQM (dotted line) predictions. See Ref. 72 regarding units of the TI EQM results.

with the exact result. The most significant discrepancy is found between the SQM prediction and the TI EQM DCS for the case of the reaction initiated from the ground vibrational state of the reactant $\text{O}_2(v=0,j=1)$: The SQM result is clearly larger and display a forward-backward propensity which is not present in neither the exact nor MPPST angular cross section. It is worth mentioning though, that as indicated in the ordinate axis of the figure, the total magnitude of the angular distributions is almost negligible due to the proximity to the reaction threshold.

A similar comparison, at a slightly higher energy $E_{\text{tot}}=0.7761$ eV, is shown in Fig. 10 for the $\text{H}+\text{O}_2(v=3,j=1)$ reaction.⁷² At this energy, the DCS is about one order of magnitude larger than the case studied in Fig. 9 for the same initial rovibrational state of the O_2 reactant. Interestingly, the differences between the two statistical approaches are now noticeably smaller than at 0.7661 eV total energy. The ob-

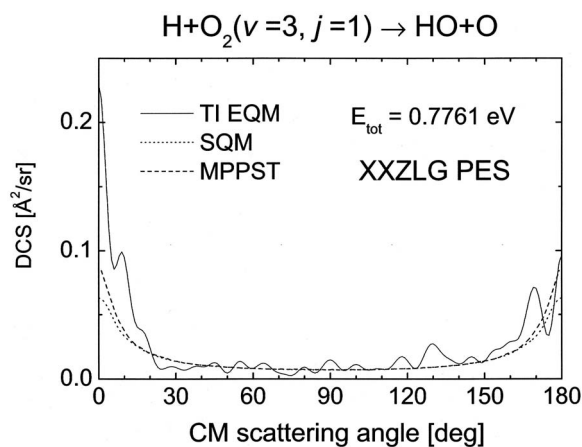


FIG. 10. Same as Fig. 8 at 0.7761 eV total energy for the reaction initiated with O₂($v=3, j=1$).

served 2.2:1 ratio between the forward and backward peaks of the exact angular distribution is logically not well described statistically, but the sideways region and the backward peak are in remarkable good accord with the TI EQM result reported in the study by Honvault *et al.*

IV. DISCUSSION

Previous EQM results have shown that probabilities for the H+O₂ reaction at not extremely large values of the total angular momentum, $J < 10$, differ significantly depending on the PES employed for the calculations.^{3,5,7} However, the comparison between the corresponding ICSs obtained on the DMBE IV and XXZLG PESs reveals that apart from the different reaction thresholds, results on both surfaces seem to be dynamically quite similar. It is difficult though to provide a complete analysis of the differences in the predicted dynamics for the H+O₂ reaction introduced by the possible different topologies of both surfaces by means of the present statistical approaches, since the intermediate region, where the collision complex is assumed to be formed, is excluded in the corresponding calculations. Beside the comparison between reaction probabilities and cross sections shown here, thermal rate constants for the title reaction and its reverse have been calculated before on both PESs by means of the wave packet version of the SQM.^{1,29} For the H+O₂→O+OH reaction, results on the DMBE IV PES and the XXZLG surface were found to be *visually indistinguishable* in the 10⁻²²–10⁻¹¹ cm³ molecule⁻¹ s⁻¹ range, whereas for the O+OH collision, statistical estimates of the rate constant were found to differ by about a factor of 3 at $T \sim 50$ K. The predictions produced here with the SQM and MPPST approaches are far from being able to describe the exact ICSs, revealing thus that the overall dynamics of the reaction cannot be reproduced statistically. In this sense, all that statistical tools are capable to reproduce seems to be restricted to an average description of the low energy range of some low J reaction probabilities for the DMBE IV surface (see Fig. 4 of Ref. 11). The analysis of state-to-state probabilities for a zero total angular momentum shows that the reason for this apparent disagreement at a higher energy regime is the propensity observed on the DMBE IV PES to produce vibrationless

OH fragments in highly excited rotational states $j' > 13$ states.^{10,11,28} This preference also explains the sudden increase of the total reactivity beyond $E_c \sim 1.25$ eV, which seems to persist somehow in the reaction probabilities up to $J \sim 5$. As the total angular momentum increases, $J > 15$, the statistical methods predict, however, too large reaction probabilities in comparison with the exact results, leading thus to the above mentioned overestimation of the ICSs.

In this sense, the XXZLG PES seemed to introduce a different dynamical scenario since the lack of the above mentioned sharp increase of reactivity would also eliminate the direct reaction channel.³ In fact, one might argue that the state-to-state probabilities for the H+O₂($v=0, j=1$)→OH($v'=0, j'$)+O processes for $J=0$ obtained with this surface were in good agreement with the corresponding statistical predictions (see Fig. 2). At least, the absence of the enhancement of certain specific rotational states to form the OH($v'=0$) product fragments could be interpreted as result of a possible statistical behavior. But any hope of such statistical dynamics on the XXZLG PES disappears as larger values of the total angular momentum are considered. Our present analysis by means of the SQM and MPPST approaches for energy values close to the reaction threshold indicates nevertheless that some of the conclusions reported on Ref. 6 might be clarified. The departure of a statistical description for the H+O₂ reaction dynamics on the XXZLG surface certainly starts as soon as the energy increases, but the correct description of the reaction thresholds by means of the SQM and MPPST methods is accompanied by statistical predictions for cross sections at those energies in a fairly good agreement with the corresponding exact results.

The comparison between the experimental cross sections and the statistical predictions deserves some further discussion. In general, SQM and MPPST ICSs are found to be larger than most of the measured values up to $E_c=1.6$ eV. At that precise collision energy, the experimental cross section is larger than what would be expected from the trend of the measurements at lower energy, which brings theory a bit closer to experiment. The interesting thing is that, although the energy range covered in Fig. 6 does not extend beyond $E_c=1.7$ eV, the reaction cross section measurements based on OH product detection reported in Refs. 67 and 68 are about 0.65 and 0.45 Å² for $E_c=1.78$ eV and $E_c=1.86$ eV, respectively. This suggests that the large value for the ICS observed at $E_c=1.6$ eV does not constitute an isolated case. If those specific measured values are not a result of any experimental artifact, the accord with the statistical prediction is certainly of interest. Besides this fairly good agreement between the calculated ICS and the corresponding measurement, the rotationally resolved distributions for the OH($v'=1$) forming channel exhibit a clear statistical profile. The above discussed different performances of the statistical calculation at the high energy regime for the two possible OH(v') channels when the DMBE IV PES is employed seems to be consistent with the distinct degree of agreement when the SQM results are compared to the experimental rotational ICSs for the two OH($v'=0, 1$)+O possible reaction products. Although we have not performed the corresponding calculation with the XXZLG PES, the observed trend for

the total ICSs in Fig. 6 leads one to think that results should not differ too much with respect to the cross sections obtained with the DMBE IV PES.

As the validity of a statistical description of the H+O₂ reaction dynamics is clearly questioned by the manifested discrepancies with the exact cross sections, one cannot rule out the possibility of an accidental agreement with the measured distributions for $E_c=1.6$ eV. Incidentally, a similar situation has been observed for some other atom-diatom processes. In particular, different statistical approaches^{73–75} have been found capable to reproduce experimental distributions for the O(³P)+HCl($v=2, j=1, 6, 9$)→OH($v'=1, j'$)+Cl reaction.^{76,77} The rotational ICSs for the product channel which leads to the formation of vibrationless OH fragments are, on the contrary, clearly not described statistically. This apparent success of the statistical tools in the comparison with the experiment contrasts, however, with the clear disagreement observed with the exact results.⁷⁸ What makes the O(³P)+HCl case even more intriguing is that the accepted dominating dynamical mechanism for the reaction is an abstraction pathway.^{74,77} This mechanism, consistent on the other hand with the absence of a deep well for the reaction, would be at odds with the use of a statistical analysis. Recently reported efforts⁷⁵ to provide some explanation for these results invoke the possible existence of a dynamical well^{79,80} which would favor the reaction for specific transitions between reactants and products. The possibility of a complex-forming mechanism is certainly based in more solid grounds for the title reaction, but as in the case of the O(³P)+HCl process, predictions obtained by means of the SQM compare quite differently to, on one hand, exact calculations and experiment and, on the other hand, to measurements resolved in different final vibrational states.

The calculations included in the present study of the H+O₂ reaction performed by means of the SQM have also shown the substantial differences introduced when the CS approximation is invoked. As largely discussed in the past^{5,29,45–47} a correct description of the Coriolis coupling terms is required. In this sense, the comparison of the SQM-CC reaction probabilities reported here to those obtained within the SQM-CS approach enables us to analyze the possible validity of such an approximation in the context of the statistical method. At a first glance, according with the results shown in Figs. 4 and 5 one could conclude that the SQM-CS predictions for the probabilities do not constitute an extremely poor alternative to the more computationally expensive SQM-CC calculations up to $J\sim 15$ –20. Beyond those values of the total angular momentum, severe discrepancies are found between the two approaches. In special, as evidenced in the two opacity functions analyzed at $E_c=0.9$ and 0.8 eV on the DMBE IV and XXZLG PESs, respectively (see Fig. 5), the CS approximation seems to yield an important overestimation of the reactivity for the larger values of J . These increasing differences between the CS and CC approaches as J augmentates are consistent with findings of the TDWP calculation by Meijer and Goldfield.⁴⁶ Moreover, in their calculation at $J=10$, probabilities for the reactions initiated from helicity-specified ($v=0, j=1, \Omega=0, 1^\pm$) states of the O₂ reactant calculated within the CS approximation ex-

hibited more marked differences with respect to the CC calculation that probabilities for the more averaged H+O₂($v=0, j=1$)→OH+O process. Analogously a strong dependence on the total number of helicity channels Ω included in the calculation was observed in the TDWP study by Lin *et al.*⁵ for the reaction initiated from the O₂($v=0, j=1, l=11$) and $J=12$. The large number of existing resonant peaks in the H+O₂ reaction seriously complicate the achievement of a perfect agreement between the CS and CC TDWP calculations. It should not be then surprising to observe variations with respect to the suggested possible maximum value of J for the validity of the CS approximation within the SQM scheme.

The situation for the title reaction slightly differs from the case of X+H₂ reactions, X being a C, N, O, or S atom. The issue of the validity of the CS approximation has been addressed in studies, for example, of N+H₂,^{81–83} O+H₂,⁸⁴ or C+H₂.^{85,86} Although it has been reported that such an approximate approach can introduce large errors in these processes due to the floppy intermediate XH₂ complex formed during the reaction,^{85,87,88} the comparison between CS results and those obtained by means of the corresponding exact CC calculations has revealed a notable good agreement in certain cases.^{81–84,86} Previous studies on the H₃⁺ system reveal, however, the importance of a proper description of the Coriolis coupling. This has been analyzed with some detail for the H⁺+D₂,⁸⁹ H⁺+H₂,⁹⁰ and D⁺+H₂ (Ref. 91) reactions. In the context of statistical techniques it has been recently found that the inclusion of such terms is required at the state-to-state level.⁵³

The clear nonstatistical features exhibited by the overall dynamics of the H+O₂ reaction preclude us from drawing firm conclusions about the existence of a dominating complex-forming mechanism for the process. The partial success of the SQM and MPPST approaches to reproduce the reaction probabilities for low values of J , and the fairly good agreement of the statistical predictions for DCSs at low energy could be signals of short living resonances.

V. CONCLUSIONS

The comparison between exact results and statistical predictions obtained by means of a SQM and a MPPST approach suggests that the H+O₂ reaction is not governed by a complex-forming mechanism. In particular, statistical ICSs have been found to seriously overestimate EQM results, with the only exception of the energy region close to the reaction threshold. Experimental cross sections are not either well reproduced statistically. At 1.6 eV collision energy, however, both the total ICS and the distributions for H+O₂($v=0, j=1$)→OH($v'=1, j'$)+O are in a remarkably good agreement with the statistical result.

As previously found in EQM calculations, the application of the CS approximation to the SQM yields significant deviations from the reactivity predicted by means of the corresponding CC calculation.

The only differences observed between the statistical results obtained on the DMBE IV and the XXZLG PESs seem

to reduce to a moderate larger degree of success of the statistical methods to reproduce reaction probabilities for low values of the total angular momentum for the DMBE IV surface.

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- ⁷¹Table II of Ref. 19 with the values for the parameters used in the least squares fit to the analytical expression $\sigma_r(E_c) = C(E_c - E_{\text{thr}})^n \exp[-m(E_c - E_{\text{thr}})]$ [from Eq. (5) of the same work] is likely to contain some typo in the case of the QCT-QMT, QCT-IEQMT, and QCT-VEQMT variants. Functions shown in Fig. 8 for these cases have been obtained by means of a similar fitting procedure of the corresponding QCT values for the ICS for $E_c < 1.5$ eV to the same expression with the following values for the parameters: $C=0.0215$, $m=0.00175$, $n=0.50964$, and $E_{\text{thr}}=63.8$ for the QCT-QMT case, $C=0.0218$, $m=0.01441$, $n=1.28596$, and $E_{\text{thr}}=67.5$ for the QCT-IEQMT case, and $C=0.00014$, $m=0.01354$, $n=1.84491$, and $E_{\text{thr}}=72.0$ for the QCT-VEQMT variant, where units for C are $\text{\AA}^2/(\text{kJ mol}^{-1})^n$, $(\text{kJ mol}^{-1})^{-1}$ for m , kJ mol^{-1} for E_{thr} , and n is a dimensionless parameter.
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