The dynamics of the $C(^1D)+H_2/D_2/HD$ reactions at low temperature

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We present results of a theoretical investigation on the dynamics of the $C(^1D)+H_2$ reaction and the corresponding isotopic variants in which the carbon atom collides either with D_2 or HD . Statistical techniques have been tested in comparison with recent experimental information at low temperature ($T < 300$ K) and exact quantum mechanical calculations reported on the title reactions in an attempt to establish their possible complex-forming character. Our study includes the calculation of probabilities, rotational distributions, integral cross sections, differential cross sections and rate constants. Previous quantum mechanical results have been extended here to complete the analysis of the underlying mechanisms which govern the collision process.

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I. INTRODUCTION

Recent investigations on the $C(^1D)+H_2$ reaction and its isotopic variants have renewed the interest on a process which has been studied extensively in the past. [1–20] On the theoretical side new potential energy surfaces (PESs) have been developed [21–23]. In particular, the *ab initio* ZMB-a surface reported by Zhang *et al.* [23] for the $1^1A'$ state of the reaction includes the accurate description of barriers induced by conical intersections between the $1^1A'$ and $2^1A'$ states at linear HCH and CHH configurations besides van der Waals (vdW) features at the entrance and exit channels. Some of these features are absent in previous PESs such as the BHL surface from Ref. [24] and its corrected form, the RKHS surface [3], and subtle differences in dynamical effects at low collision energies can be noticed [25]. The ZMB-a PES has been employed in theoretical studies of the $C(^1D)+H_2$ reaction [26] and the $C(^1D)+D_2$ [25] and $C(^1D)+HD$ [27, 28] isotopic variants. On the experimental side, rate coefficients at low temperatures (50–300 K) have been recently obtained by means of supersonic flow reactor investigations for the collision of a carbon atom both with H_2 [29] and D_2 [30].

One of the issues treated on these works deals with the actual participation of excited electronic states on the overall reactivity of the process. Real wave packet (RWP) calculations [15] performed both on the ground $1^1A'$ [24] and first excited $1^1A''$ [9] states revealed that different dynamical pathways are associated to each PES for the $C(^1D)+H_2$ reaction. In particular the lower surface was found to favor an

indirect perpendicular approach of the carbon atom whereas on the $1^1A''$ state a direct sideways insertion is the preferred mechanism. The contribution of this latter surface to the thermal rate constant accounts for about 40% between 100 and 500 K, with a final value at the room temperature in a reasonably good agreement with experimental values [31]. The rate constants calculated by means of a ring-polymer molecular dynamics (RMPD) method [32] for the $C(^1D)+H_2$ [30] and $C(^1D)+D_2$ [29] reactions on the excited $1^1A''$ PES are larger than those obtained on the ground electronic state. Rate constants and integral cross sections (ICS) were also calculated employing both uncoupled PESs for the $C(^1D)+HD$ and $C(^1D)+D_2$ reactions [16]. A Renner-Teller coupled-channel investigation of the dynamics for the title reaction with both surfaces [17] yielded smaller rate constants with a positive dependence with the temperature. Adiabatical quantum mechanical (QM) and quasi-classical trajectory (QCT) calculations [13] concluded that the participation of the first excited $1^1A''$ PES does not improve the minor discrepancies previously observed between theoretical simulations of laboratory angular and time-of-flight distributions obtained on the ground state PES with respect to the experimental results [18]. Balucani *et al.* [18] found that, contrary as expected, the contribution of such excited state worsens the agreement with the measured distributions.

Previous investigations suggest that the overall dynamics of the reaction is governed by a complex-forming mechanism. Thus, the preference for the formation of CH in its ground vibrational state, the inversion of the corresponding rotational distributions of $CH(v' = 0, j')$ and the predominantly forward-backward symmetry of the differential cross sections (DCSS) reported in the study by Shen *et al.* [26] of the $C(^1D)+H_2$ reaction seem to correspond to such dynamics. This symme-

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try around the sideways ($\theta \sim 90^\circ$) direction which leads to almost identical peaks along the forward ($\theta \sim 0^\circ$) and backward ($\theta \sim 180^\circ$) scattering directions was also observed in a similar study for the $C(^1D)+D_2$ reaction [25]. One of the conclusive tests to establish the importance of the complex-forming pathway in atom-diatom reactions is the application of statistically-based approximative approaches which assume the formation of an intermediate species between reactants and products. The comparison of statistical predictions with both exact QM (EQM) and experimental results has been a useful approach in the past for a large series of reactions. As far as we know this is the first attempt to reproduce some of the most recent information we have from the title reaction reported in theoretical and experimental studies by means of statistical techniques. In particular we have applied the statistical quantum mechanical (SQM) method developed by Manolopoulos and coworkers [33, 34] and mean potential phase space theory (MPPST) [35–37]. These approaches have been employed before to study the title reaction and isotopic variants [10, 11, 33, 37–40] providing valuable information about the dynamics of the process. In this work we employ these statistical techniques on two of the most commonly used PESs (the ZMB-a [23] and RKHS [3]) to investigate the role played by the complex-forming mechanisms in this reaction. We have also performed EQM calculations with the RWP method of Ref. [25] to complete the investigation on the $C(^1D)+D_2$ reaction calculating ICS at lower energies, rotational and differential cross sections.

The structure of the paper is the following: In Section II details of the three theoretical approaches employed in this work are given; results are shown and discussed in Section III and finally conclusions are in Section IV.

II. THEORY

A. Statistical Quantum Mechanical Method

The SQM approach assumes that the reaction takes place by means of the formation of an intermediate complex between reactants and products. Thus the state-to-state reaction probability at the total angular momentum J between the initial (v, j) rovibrational state of the reactant diatom and the final (v', j') state of the corresponding diatomic product molecule can be approximated as [33, 34]:

$$P_{vj,v'j'}^J(E) \simeq \frac{p_{vj}^J(E)p_{v'j'}^J(E)}{\sum_{v''j''} p_{v''j''}^J(E)}, \quad (1)$$

where $p_{v'j'}^J(E)$ and $p_{vj}^J(E)$ are the capture probabilities for the formation and fragmentation, respectively of the intermediate species, and the indexes in the sum of the denominator, $v''j''$, run over all the energetically open rovibrational states both in reactants and products. Those individual probabilities are calculated by means of a time-independent method explained before [33, 34] involving a log derivative propagation between a capture radius R_c and an asymptotic distance $R_{\max}$. The values

of these two parameters in the present calculations were set to $\sim 3 \text{ \AA}$ and $\sim 50 \text{ \AA}$, respectively for the reactant channels of the three reactions under study. For the corresponding product channels, R_c was taken $\sim 4 \text{ \AA}$ in all cases whereas $R_{\max}$ could vary between the $\sim 60 \text{ \AA}$ of the $D+CH$ case and $\sim 80 \text{ \AA}$ of the $H+CD$ case. As in previous investigations with the SQM method of the title reactions [10, 11, 33] the calculations are performed within the centrifugal sudden approximation.

The reaction probability of Equation (1) to calculate ICSs, $\sigma_{vj,v'j'}(E)$, and then rate constants as follows:

$$k_{vj,v'j'}(T) = \sqrt{\frac{8\beta^3}{\pi\mu}} \int_0^\infty \sigma_{vj,v'j'}(E) e^{-\beta E} dE, \quad (2)$$

where μ is the system reduced mass and $\beta = (k_B T)^{-1}$. As explained before [33], the calculation of DCSs requires the random phase approximation to give:

$$\sigma_{vj,v'j'}(\theta, E) \simeq \frac{1}{8k_{vj}^2(2j+1)} \sum_{J\Omega\Omega'} (2J+1)^2 \Xi^J(\theta) P_{vj,v'j'}^J(E) \quad (3)$$

where we have defined $\Xi^J(\theta) = |d_{\Omega\Omega'}^J(\pi - \theta)|^2 + |d_{\Omega\Omega'}^J(\theta)|^2$ and $k_{vj}^2 = 2\mu(E - E_{vj})/\hbar^2$ is the wave vector in the reactant channel.

B. Mean Potential Phase Space Theory

The MPPST constitutes a semi-classical statistical approach to tackle the study of atom-diatom reactions [37, 38] with the same basic assumption of an intermediate complex as in the SQM explained in the previous section. Individual probabilities for the asymptotic semiclassically quantized (v, j, ℓ) states to use in Equation (1) are calculated in an approximate manner via a two-body capture model [41] accounting for the tunnelling by means of the WKB model [42] through the radial effective potential obtained by averaging over the reactant γ Jacobi coordinate. Such an averaging implicitly accounts for the moderate anisotropies involved in complex-formation dynamics for barrierless processes at low collision energies. In the present implementation, internal states of both reactant and product channels are treated as rigid rotor anharmonic oscillator [43]. The isotropic assumption for the inter-fragment potential produces capture cross section which do not depend on the initial rotational state of the reactant diatom.

C. Exact Quantum Mechanical Method

The quantum dynamics calculations including all Coriolis couplings were performed using the RWP approach as implemented in the DIFFREALWAVE code [44, 45]. Some of the results we employ here for comparison with the statistical predictions have already been published elsewhere but for the $C(^1D)+D_2 \rightarrow CD + D$ reaction, more cross sections and

DCSs have been calculated here in order to complete previous investigations. The wave packet (WP) is initially located at the reactant channel with its center R_0 at sufficiently large values in the asymptotic region to include the long range interactions. In order to obtain state-to-state quantities, it is then transformed in terms of product Jacobi coordinates: r' for the C–D distance, R' for the distance between the remaining D atom and the center of mass of the CD diatom and γ' the angle between these two radial vectors. The analysis line R'_∞ where the WP is cut at each time step of the Chebyshev iteration is chosen in the product asymptotic region where the potential is as flat as possible. Whereas for small values of the total angular momentum these criteria are easily satisfied, when J increases the centrifugal potential falls off slower and, therefore, R_0 and R'_∞ must take sufficiently large values. The numerical values of some of these parameters employed in the calculation are those from Ref. [25]. Furthermore, test calculations about the absorption strength, center of the initial WP and width of the WP have been performed to make sure that the results at low collision energies are converged.

The expression of the DCS is given by:

$$\sigma_{v_j, v' j'}(\theta, E) = \frac{1}{2j+1} \sum_{\Omega \Omega'} \frac{1}{4k_{vj}^2} \times \left| \sum_J (2J+1) S_{vj\Omega, v' j'\Omega'}^J(E) d_{\Omega \Omega'}^J(\theta) \right|^2 \quad (4)$$

The $\mathbf{S}$ matrix of the above equation (4) is in the body-fixed frame but it is initially calculated in the space-fixed (SF) reference system to avoid the Coriolis coupling terms and to take advantage of the fact that the corresponding (ℓ, j) channels in that frame are not subjected to any long range coupling [44]. As explained in detail in Ref. [44] the phase of the scattering matrix in the SF representation must also include some correction terms due to the nonzero values of the centrifugal potential at R'_∞ .

The corresponding ICSs are then obtained by integration of the DCS in Equation (4) over the angular coordinates:

$$\sigma_{v_j, v' j'}(E) = 2\pi \int_0^\infty \sin\theta \sigma_{v_j, v' j'}(\theta, E) d\theta = \frac{\pi}{k_{vj}^2} \sum_{\Omega \Omega'} \sum_J (2J+1) \left| S_{vj\Omega, v' j'\Omega'}^J(E) \right|^2 \quad (5)$$

For the analysis of the WP final vibrational states up to $v' = 2$ and rotational states up to $j' = 24$ were considered.

III. RESULTS

A. Integral Cross Sections

ICSs calculated by means of the SQM approach on the ZMB-a and RKHS PESs for the $C(^1D)+H_2$ reactions shown in Figure 1 exhibit some of the differences mentioned in previous investigations between the dynamics predicted on both

FIG. 1: ICSs for $C(^1D)+H_2$ as a function of the collision energy. Black and blue lines correspond to calculations performed on the ZMB [23] and RKHS PES [3], respectively. Solid lines are EQM results reported in Ref. [26] (black) and [12] (blue). SQM and MPPST results are shown in dashed-dotted and dotted lines.

surfaces. The analysis performed by Shen *et al.* [25] reveals that vdW features in the entrance channel on the ZMB-a surface enhances reactivity thus leading to larger ICSs, whereas trajectories on the RKHS surface may suffer back reflection and thus do not contribute as much to the total reactivity. Consistent with these findings, the statistical cross sections for the RKHS PES shown in Figure 1 down to 5×10^{-4} eV are clearly smaller than those obtained on the ZMB-a surface. Results obtained in the time dependent wave packet (TDWP) calculation of Liu *et al.* [12] on the RKHS PES and the RWP study by Shen *et al.* [26] on the ZMB-a surface for the $C(^1D)+H_2$ reaction (also included in Figure 1) do not extend below 3×10^{-3} eV. The EQM results, reasonably well described by the statistical predictions in that energy regime, show nevertheless the above mentioned discrepancies between PESs, and in particular, the TDWP approach on the RKHS surface seems to suggest a similar behaviour as the SQM prediction. **The MPPST cross sections obtained using both surfaces exhibit qualitatively the same behaviour, especially at low energies ($E_c < 10^{-2}$ eV). The differences with respect to the SQM predictions disappear for $E_c > 4 \times 10^{-3}$ eV. The origin of such discrepancies, also observed for the $C(^1D)+D_2$ reaction, is discussed below.**

For the $C(^1D)+D_2$ reaction, on the contrary, it has been possible to establish the comparison between exact and statistical cross sections for much lower energies. In particular, we have used the EQM method of Section II C to calculate ICSs below $E_c \sim 10^{-3}$, thus extending the cross sections previously shown in Ref. [25] below 6×10^{-4} eV, and the results are compared in Figure 2 with the SQM and MPPST predictions. The agreement between both sets of results is certainly remarkable thus suggesting that the dynamics of the reaction at such low energies can be mediated by the formation of an intermediate complex CD_2 . The only differences are found when the energy increases where the statistical approaches, especially the SQM results, seem to slightly overestimate the

FIG. 2: ICSs for the $C(^1D)+D_2$ reaction as a function of the collision energy. Black and blue lines correspond to calculations performed on the ZMB [23] and RKHS PES [3], respectively. EQM results (solid lines) are from Ref. [25] but have been extended for this work to lower energies in the case of the ZMB PES (black line). SQM and MPPST results are shown in dashed-dotted and dotted lines. Red squares are experimental results from Liu [14] scaled to match SQM value at 0.1 eV.

FIG. 3: Same as Figs. 1 and 2 for the $C(^1D)+HD$ reaction. Solid lines are for the CD+H formation product arrangement and dashed lines are for the CH+D exit channel. EQM results [27] (black lines) are compared with present SQM (red lines) and MPPST results (blue lines).

EQM cross sections. The calculations on the RKHS PES produce similar results as the case of $C(^1D)+H_2$ (see Figure 1): the statistical ICSs stay somehow larger than the EQM result from Ref. [25] (reported only for $E_c > 10^{-2}$ eV) and below $\sim 4 \times 10^{-4}$ eV the SQM ICSs decrease noticeably with respect to the MPPST values as the energy becomes lower. The different behaviour of the cross sections depending on the specific PES employed in the calculations was already reported for $C(^1D)+D_2$ by Shen *et al.* [25]. The authors claimed that the improvements introduced in the ZMB-a surface regarding the

van der Waals region in the entrance valley make, for instance, that classical trajectories react to produce CD+D instead of back scattering as found on the RKHS surface. This dynamical feature is thus consistent with the pronounced decrease also seen in the EQM calculation as the energy diminishes (see Fig. 1 for the $C(^1D)+H_2$ reaction where the corresponding EQM result is extended to a larger range of low energy). In this sense, the reproduction of such behaviour by means of the SQM approach indicates that the choice of the corresponding capture radius allows the method to experience the different topologies of both the ZMB-a and RKHS PESs in the van der Waals region. The MPPST method in turn employs larger values of the capture radius when the collision energy decreases due to the displacement of the centrifugal barriers to further distances. As a result, the region of the potential effectively assumed as a well in the MPPST calculation does not include the repulsive features in the RKHS PES which are absent from the ZMB-a. The excitation functions measured in the crossed-beam study by Liu [14], also included in the figure scaled to match the SQM values at a collision energy $E_c \approx 0.1$ eV, exhibit certain differences at the low energy but, as stated in Ref. [25], the overall theory versus experiment comparison is already reasonably good without including the $1A''$ PES in the calculation in view of the experimental uncertainties.

The ratio between the cross sections of the CD produced in its first excited vibrational state and in its ground state, $CD(v' = 1)/CD(v' = 0)$, can be also described quite accurately by means of statistical techniques. In Table I the values reported in the RWP calculation by Shen *et al.* [25] are compared with ratios obtained in this work with both the SMQ and MPPST approaches as a function of the collision energy. Some slight deviations are only noticeable as the energy increases beyond 0.20 eV, but below, the agreement between both methods is remarkable. It is worth noticing that the ratios obtained in the MPPST calculation could be even improved by extracting the energy levels directly from the *ab initio* PES instead of through an estimation under the anharmonic oscillator rigid rotor assumption for the involved diatomic fragments. The crossed beam measurement reported by Balucani *et al.* [11] remains however too small with respect to the theoretical values. As for the case of the ICSs discussed above, Shen *et al.* [25] showed that the contribution of the excited electronic state $1A''$ makes the EQM $CD(v' = 1)/CD(v' = 0)$ ratio decreases significantly leading to a much better accord with the experimental value at $E_c \approx 0.161$ eV.

A similar investigation on the $C(^1D)+HD$ reaction reveals more intriguing deviations from a statistical description, more precisely for the CD+H formation. Thus, the comparison shown in Figure 3 indicates that both SQM and MPPST ICSs differ somehow from those reported in the RWP study by Sun *et al.* [27] when the energy increases. In this sense, only the SQM cross sections seem to suggest the trend exhibited by the EQM ICS beyond $E_c \sim 0.4$ eV. Below $E_c = 10^{-2}$ eV, however, both statistical cross sections agree quite well. For that lower energy range, much more computationally demanding for time dependent techniques, there are no results from Ref. [27], but the accord among the three sets of data in Figure 3 for both the CD+H and CH+D product channels, suggest the

TABLE I: $CD(v' = 1)/CD(v' = 0)$ ratio between the ICS to produce CD in its vibrational first excited and ground states in the $C(^1D)+D_2 \rightarrow CD+D$ reaction as a function of the collision energy in eV (first column) according to EQM results of Ref. [25] (second column), SQM (third column) and MPPST (fourth) values of this work. The experimental value is from the crossed beam investigation of Ref. [11].

E_c	EQM	SQM	MPPST	EXP
0.05	0.012	0.014	0.054	
0.10	0.088	0.100	0.173	
0.15	0.197	0.193	0.269	
0.161	0.213	0.210	0.292	0.11
0.20	0.300	0.272	0.358	
0.25	0.403	0.331	0.427	
0.30	0.452	0.386	0.488	

good performance of the statistical results.

B. Rotational Distributions

FIG. 4: Rotational cross sections for $C(^1D)+H_2 \rightarrow CH(v', j')+H$ at $E_c = 80$ meV (top panel) and 320 meV (bottom panel). EQM results (black squares) [23] are compared with present SQM (red circles) and MPPST (blue triangles) distributions.

A description at a state-to-state level can be achieved by the analysis of the rotational cross sections. In particular, the statistical distributions for the $C(^1D)+H_2(v = 0, j = 0) \rightarrow CH(v', j')+H$ reaction at $E_c = 0.08$ and 0.32 eV are compared in Figure 4 with the EQM results reported in Ref. [26]. The profile of hot distributions favouring the population of

FIG. 5: Same as Fig. 4 for $C(^1D)+D_2 \rightarrow CD(v', j')+D$ at $E_c = 80$ meV. All results are from this work.

the excited rotational $CH(v', j')$ states is typical of a complex-forming mechanism and therefore it should not surprise that both the SQM and MPPST approaches manage to reproduce satisfactorily the EQM results. It may be argued that, in the case of the largest energy, 0.32 eV, the agreement looks better for the production of $CH(v' = 1, j')$ in its vibrationally excited state than for the formation in its ground state, but it is fair to point out the good overall performance of the statistical description of the product rotational distributions.

In order to extend such a comparison to the case of the $C(^1D)+D_2$ reaction, we have obtained the rotational distributions at $E_c = 0.08$ eV via a RWP calculation as in Ref. [25]. The comparison between the EQM rotational cross sections and those predicted by means of the statistical methods employed here is shown in Figure 5. CD is formed at this energy in both its ground $CD(v' = 0)$ and first $CD(v' = 1)$ vibrational states and whereas for $v' = 0$ we find pretty much the same situation as the case of $C(^1D)+H_2$ extended to larger rotational states ($j' = 18$), all the corresponding $CD(v' = 1, j')$ states seem to be populated according to statistical considerations, as revealed by the comparison with the SQM and MPPST distributions.

C. Differential Cross Sections

One of the most extensively analyzed issues in the recent investigation of the $C(^1D)+H_2$ reaction by Shen *et al.* [26] is the DCSs as a function of the collision energy. It was found that in general, the backward-forward ratio remains close to unity especially for the largest partial waves contributing to the reaction. The symmetry between the forward and backward peaks of the DCSs is a well known distinctive feature of an insertion dynamics mediated by the formation of an intermediate species between reactants and products. In fact previous comparisons between statistically obtained angular distributions and EQM DCSs have revealed that the title reactions behave in essence as one of such a complex-forming process [10, 33]. In Figure 6 we present DCSs for (a) $C(^1D)+H_2$,

FIG. 6: Comparison of EQM (black lines), SQM (red lines) and MPPST (blue lines) DCSs for the (a) $C(^1D)+H_2$ and (b) $C(^1D)+D_2$ reactions at $E_c = 80 \text{ meV}$. EQM results in (a) are taken from Ref. [23] and have been calculated here in this work for (b).

and (b) $C(^1D)+D_2$ at 0.08 eV collision energy obtained on the ZMB-a PES. Previous results at the same energy with the RKHS surface revealed that the specific PES employed in the calculation does not introduce significant differences. The DCS is well described for both reactions by the statistical approach, with a slightly better agreement in the case of $C(^1D)+H_2$ which exhibits a larger symmetry around the sideways scattering direction.

We have also carried out both SQM and MPPST calculations to compare with DCSs for the $C(^1D)+H_2(v=0, j=0) \rightarrow CH(v'=0, j')+H$ processes investigated in Ref. [26] at 0.08 eV. The formation of $CH(v'=0, j')$ at some specific final rotational states, $j' = 1, 5$ and 12 , have been considered and the comparison with the RWP DCSs reported by Shen *et al.* [26] shown in Figure 7 reveals a remarkably good agreement. For some other cases not shown here (such as, for example, $j' = 3, 6$ or 13) the EQM distributions exhibit pronounced peaks at both the forward and backward scattering directions that the statistical predictions do not reproduce satisfactorily. In this sense it is worth noticing that although the state-to-state level does not constitute a valid scenario to test a statistical technique [46, 47], the overall accord with the EQM results is certainly good.

D. Rate Constants

Some of the most recent information published on the title reaction addresses the behaviour of the rate constant at low

FIG. 7: State-to-state DCS for the $C(^1D)+H_2(v=0, j=0) \rightarrow CH(v'=0, j')+H$ reaction at $E_c = 80 \text{ meV}$ for $j' = 1$ (top panel), $j' = 5$ (middle panel) and $j' = 12$ (bottom panel). Comparison between EQM results from Ref. [26] (black lines) and present statistical predictions: SQM in red and MPPST in blue lines.

temperature. Figure 8 and 9 show experimental rates by Hickson and collaborators for $C(^1D)+H_2$ [29] and $C(^1D)+D_2$ [30] between 50 and 300 K. The SQM predictions provide a good theoretical counterpart when the contribution of the excited $1A''$ electronic state (taken from Ref. [9]) is included, specially for the $C(^1D)+H_2$ reaction (see Figure 8). The MPPST rates, on the contrary, overestimates the most recent experimental work on this latter reaction, with values which remain close to the upper limit of the error bars of the measurements by Hickson *et al.* [29]. Both statistical approaches produce rate constants which slightly overestimate the experimental values for $C(^1D)+D_2$ (see Figure 9). For this reaction, EQM results from the RWP calculation by Shen *et al.* [25] agree very well with the experimental value of the rate coefficient at the room temperature and the extrapolation to a lower temperature regime seems to also reproduce correctly the measurements reported in Ref. [30]. In general, the comparison of those new measurements with theoretical calculations of the rate constants reveals the necessity of the $1A''$ PES since the estimations performed solely on the ground electronic state $1A'$ are clearly below the experimental values, agreeing only with older data such as those reported by Sato *et al.* [31]. This ($1A' + 1A''$)-calculation remains, on the other hand, be-

FIG. 8: Rate constants for the $C(^1D)+H_2$ reaction obtained with the SQM and MPPST approaches on the ZMB (dashed-dotted line), on the $1A'$ (dashed line) and $1A' + 1A''$ (solid line) RKHS PESs. EQM values obtained on the ZMB PES (black dashed-dotted line) are from Ref. [26] and on the RKHS PES (black dashed line) from the TDWP calculation of Ref. [12]. Experimental results by Sato *et al.* [31] (green square), by Fisher *et al.* [48] (magenta square), by Husain *et al.* [49] (open diamond) and from Ref [29] (black triangles) are included for comparison.

tween the room temperature rate constant by Fisher *et al.* [48] and that measured by Husain and Kirsch [49]. In addition, and consistent with the previously discussed different reactivity between the two surfaces, the thermal coefficients obtained with the ZMB-a PES are larger than those calculated on the RKHS PES. These differences are manifested both in the EQM and statistical calculations (see Figures 8 and 9). The contribution from the excited state, crucial to match the experiment at the low temperature regime, is also responsible, in the case of the SQM predictions, of certain degree of negative dependence of the rate constant. Thus, whereas the statistical result for $C(^1D)+H_2$ on the ground electronic state increases at low T with increasing temperature before reaching a plateau, the addition of the $1A''$ (not shown here) leads to the almost T -independent profile.

Interestingly certain negative dependence is observed in the EQM rate constant shown in Figure 9 for the $C(^1D)+D_2$ reaction, a behaviour which is also present in the thermal coefficients of the WP calculations by Defazio *et al.* [16] for $C(^1D)+HD$. As shown in Figure 10 results for both product channels of the $C(^1D)+HD$ collision from Sun *et al.* [27] exhibit, on the contrary, an intrinsically different dependence with the temperature which is qualitatively similar to the trend of the statistical results. Both SQM and MPPST approaches predict nevertheless rate constants for $C(^1D)+HD \rightarrow CD+H$ which are quantitatively close to the result from Ref. [16]. In addition to this, statistical rates are found to be in a better agreement with those reported from Ref. [27] for $C(^1D)+HD \rightarrow CH+D$.

The apparently anomalous situation found for the

FIG. 9: Comparison of rate constants for the $C(^1D)+D_2$ reaction obtained using the ground ZMB-a PES (dashed lines) and on both $1A'$ and $1A''$ PES (solid lines) by means of the EQM (black lines) -adapted from supplementary material of Ref. [25] and completed for this work-, SQM (red lines) and MPPST (blue lines). The experimental results by Sato *et al.* [31] (green square), by Fisher *et al.* [48] (magenta square) and by Hickson *et al.* [30] (black triangles) are included for comparison.

TABLE II: $k_{CD}(T)/k_{CH}(T)$ ratio between the rate constants corresponding to the $C(^1D)+HD \rightarrow CD+H$ and $C(^1D)+HD \rightarrow CH+D$ reactions as a function of the temperature in K. In second column, results from the WP calculations of Ref. [27]; third column are the SQM results of this work, fourth column are present MPPST results and in the fifth column the QCT ratios from Ref. [50].

T	EQM	SQM	MPPST	QCT
100	1.476	1.848	2.015	2.124
200	1.369	1.863	2.032	2.087
300	1.319	1.861	2.05	2.062
400	1.297	1.856	2.062	2.036
500	1.298	1.848	2.069	2.022

$C(^1D)+HD$ reaction is also manifested in the comparison shown in Table II of the ratio between the thermal rate constants for both product arrangements, $CH+D$ and $CD+H$. The SQM results are just in between those reported in the RWP calculation by Sun *et al.* [27] and the QCT calculations performed on a different PES by Joseph *et al.* [50]. MPPST on the other hand, somehow larger than those obtained by means of the SQM approach, are closer to results from that latter QCT investigation. Given the reasonably good performance of the statistical approaches here employed in the case of the $C(^1D)+H_2/D_2$ reactions, we are tempted to point out the existence of possible deficiencies in the EQM calculations of Ref. [27]. In this sense it might be argued that both the range of the r coordinate and of the absorbing potential are not sufficiently large in the RWP calculations performed by Sun *et al.*. Whether or not that could be the case would have to be

FIG. 10: Rate constants for the $C(^1D)+HD \rightarrow CD+H$ (solid lines) and $C(^1D)+HD \rightarrow CH+D$ (dashed-dotted lines) reactions. EQM^a results (black lines) are from Ref. [27] and EQM^b (green lines) are from Ref. [16]. SQM (red lines) and MPPST (blue lines) rates are also compared with the experimental values by Sato *et al.* [31] (triangles) for both product channels.

ultimately checked by a similar EQM calculation.

IV. CONCLUSIONS

Our study explores the dynamics of the title reactions by means of quantum and statistical techniques in an attempt to understand recent theoretical and experimental work at low temperature and energy regimes. Besides an extensive statistical investigation, results from a EQM calculation on the $C(^1D)+D_2$ reaction are presented, including integral cross sections at lower energies, rotational distributions and DCSs. Our conclusions are that in view of the fairly good performance of techniques such as the presently employed SQM and MPPST methods, which assume the formation of an intermediate complex between reactants and products, the dynamics of the $C(^1D)+H_2$ reaction and isotopic variants seems to be mainly ruled by an insertion mechanism.

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- [1] K. Mikulecky and K. Gericke, *J. Chem. Phys.* **98**, 1244 (1993).
 - [2] A. Bergeat, L. Cartechini, N. Balucani, G. Capozza, L. Phillips, P. Casavecchia, G. Volpi, L. Bonnet, and J.-C. Rayez, *Chem. Phys. Lett.* **327**, 197 (2000).
 - [3] L. Bañares, F. Aoiz, S. A. Vázquez, T.-S. Ho, and H. Rabitz, *Chem. Phys. Lett.* **374**, 243 (2003).
 - [4] S. Lin and H. Guo, *J. Chem. Phys.* **119**, 11602 (2003).
 - [5] S. Lin and H. Guo, *J. Phys. Chem. A* **108**, 10066 (2004).
 - [6] S. Lin and H. Guo, *J. Phys. Chem. A* **108**, 2141 (2004).
 - [7] S. Lin and H. Guo, *J. Chem. Phys.* **121**, 1285 (2004).
 - [8] L. Mouret, J.-M. Launay, M. Terao-Dunseath, and K. Dunseath, *Phys. Chem. Chem. Phys.* **6**, 4105 (2004).
 - [9] B. Bussery-Honvault, J. Julien, P. Honvault, and J.-M. Launay, *Phys. Chem. Chem. Phys.* **7**, 1476 (2005).
 - [10] T. González-Lezana, *Int. Rev. Phys. Chem.* **26**, 29 (2007).
 - [11] N. Balucani, G. Capozza, E. Segoloni, A. Russo, R. Bobbenkamp, P. Casavecchia, T. González-Lezana, E. J. Rackham, L. Bañares, and F. J. Aoiz, *J. Chem. Phys.* **122**, 234309 (2005).
 - [12] J. Liu, B. Fu, and D. Zhang, *Chem. Phys. Lett.* **480**, 46 (2009).
 - [13] N. Balucani, P. Casavecchia, F. Aoiz, L. Bañares, J.-M. Launay, B. Bussery-Honvault, and P. Honvault, *Mol. Phys.* **108**, 373 (2010).
 - [14] K. Liu, *Int. Rev. Phys. Chem.* **20**, 189 (2001).
 - [15] P. Defazio, C. Petrongolo, B. Bussery-Honvault, and P. Honvault, *J. Chem. Phys.* **131**, 114303 (2009).
 - [16] P. Defazio, P. Gamallo, M. González, S. Akpınar, B. Bussery-Honvault, P. Honvault, and C. Petrongolo, *J. Chem. Phys.* **132**, 104306 (2010).
 - [17] P. Defazio, B. Bussery-Honvault, P. Honvault, and C. Petrongolo, *J. Chem. Phys.* **135**, 114308 (2011).
 - [18] N. Balucani, G. Capozza, L. Cartechini, A. Bergeat, R. Bobbenkamp, P. Casavecchia, F. J. Aoiz, L. Bañares, P. Honvault, B. Bussery-Honvault, et al., *Phys. Chem. Chem. Phys.* **6**, 4957 (2004).
 - [19] L. Bañares, F. Aoiz, P. Honvault, B. Bussery-Honvault, and J. Launay, *J. Chem. Phys.* **118**, 565 (2003).
 - [20] P. Honvault, B. Bussery-Honvault, J. Launay, F. Aoiz, and L. Bañares, *J. Chem. Phys.* **124** (2006).
 - [21] X. Liu, W. Bian, X. Zhao, and X. Tao, *J. Chem. Phys.* **125**, 074306 (2006).
 - [22] Y. Wu, C. Zhang, J. Cao, and W. Bian, *J. Phys. Chem. A* **118**, 4235 (2014).
 - [23] C. Zhang, M. Fu, Z. Shen, H. Ma, and W. Bian, *J. Chem. Phys.* **140**, 234301 (2014).
 - [24] B. Bussery-Honvault, P. Honvault, and J.-M. Launay, *J. Chem. Phys.* **115**, 10701 (2001).
 - [25] Z. Shen, H. Ma, C. Zhang, M. Fu, Y. Wu, W. Bian, and J. Cao, *Nature Comm.* **8**, 14094 (2017).
 - [26] Z. Shen, J. Cao, and W. Bian, *J. Chem. Phys.* **142**, 164309 (2015).
 - [27] Z.-P. Sun, W.-K. Zhao, and C.-L. Yang, *Int. J. Quant. Chem.* **117**, e25431 (2017).
 - [28] C. Zhang, Y. Zheng, J. Cao, and W. Bian, *RSC Adv.* **7**, 34348 (2017).
 - [29] K. M. Hickson, J.-C. Loison, H. Guo, and Y. V. Suleimanov, *J. Phys. Chem. Lett.* **6**, 4194 (2015).
 - [30] K. M. Hickson and Y. V. Suleimanov, *Phys. Chem. Chem. Phys.* **19**, 480 (2017).
 - [31] K. Sato, N. Ishida, T. Kurakata, A. Iwasaki, and S. Tsunashima,

- Chem. Phys. **237**, 195 (1998).
- [32] Y. V. Suleimanov, W. J. Kong, H. Guo, and W. H. Green, J. Chem. Phys. **141**, 244103 (2014).
 - [33] E. J. Rackham, T. González-Lezana, and D. E. Manolopoulos, J. Chem. Phys. **119**, 12895 (2003).
 - [34] E. J. Rackham, F. Huarte-Larrañaga, and D. E. Manolopoulos, Chem. Phys. Lett. **343**, 356 (2001).
 - [35] M. Jorfi, B. Bussery-Honvault, P. Honvault, T. Stoecklin, P. Larrégaray, and P. Halvick, J. Phys. Chem. A **114**, 7494 (2010).
 - [36] P. Larrégaray and L. Bonnet, Comp. Theor. Chem. **990**, 18 (2012).
 - [37] P. Larrégaray, L. Bonnet, and J.-C. Rayez, J. Chem. Phys. **127**, 084308 (2007).
 - [38] P. Larrégaray, L. Bonnet, and J.-C. Rayez, J. Phys. Chem. A **110**, 1552 (2006).
 - [39] L. Bonnet, P. Larrégaray, and J.-C. Rayez, Phys. Chem. Chem. Phys. **25**, 3228 (2007).
 - [40] L. Bonnet, P. Larrégaray, J. C. Rayez, and T. González-Lezana, Phys. Chem. Chem. Phys. **8**, 3951 (2006).
 - [41] P. Langevin, Ann. Chim. Phys. **5**, 245 (1905).
 - [42] R. Meana-Paneda, D. G. Truhlar, and A. Fernández-Ramos, J. Chem. Theory. Comm. **6**, 6 (2010).
 - [43] P.J. Linstrom and W.G. Mallard, Eds., NIST Chemistry Web-Book, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899 **doi:10.18434/T4D303**
 - [44] M. Hankel, S. C. Smith, R. J. Allan, S. K. Gray, and G. G. Balint-Kurti, J. Chem. Phys. **125**, 164303 (2006).
 - [45] M. Hankel, S. C. Smith, S. K. Gray, and G. G. Balint-Kurti, Comp. Phys. Comm. **179**, 569 (2008).
 - [46] T. González-Lezana, O. Roncero, P. Honvault, J.-M. Launay, N. Bulut, F. J. Aoiz, and L. Bañares, J. Chem. Phys. **125**, 094314 (2006).
 - [47] P. Larrégaray and L. Bonnet, J. Chem. Phys. **143**, 144113 (2015).
 - [48] W. Fisher, T. Carrington, C. Sadowski, and C. Dugan, Chem. Phys. **97**, 433 (1985).
 - [49] D. Husain and L. Kirsch, Chem. Phys. Lett. **9**, 412 (1971).
 - [50] S. Joseph, P. J. S. B. Caridade, and A. J. C. Varandas, J. Phys. Chem. A **115**, 7882 (2011).