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# Quantum chemical study of the reaction paths and kinetics of acetaldehyde formation on a methanol–water ice model†

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Acetaldehyde (CH<sub>3</sub>CHO) is ubiquitous in interstellar space and is important for astrochemistry as it can contribute to the formation of amino acids through reaction with nitrogen containing chemical species. Quantum chemical and reaction kinetics studies are reported for acetaldehyde formation from the chemical reaction of C(<sup>3</sup>P) with a methanol molecule adsorbed at the eighth position of a cubic water cluster. We present extensive quantum chemical calculations for total spin  $S = 1$  and  $S = 0$ . The U $\omega$ B97XD/6-311++G(2d,p) model chemistry is employed to optimize the structures, compute minimum energy paths and zero-point vibrational energies of all reaction steps. For the optimized structures, the calculated energies are refined by CCSD(T) single point computations. We identify four transition states on the triplet potential energy surface (PES), and one on the singlet PES. The reaction mechanism involves the intermediate formation of CH<sub>3</sub>OCH adsorbed on the ice cluster. The rate limiting step for forming acetaldehyde is the C–O bond breaking in CH<sub>3</sub>OCH to form adsorbed CH<sub>3</sub> and HCO. We find two positions on the reaction path where spin crossing may be possible such that acetaldehyde can form in its singlet spin state. Using variational transition-state theory with multidimensional tunnelling we provide thermal rate constants for the energetically rate limiting step for both spin states and discuss two routes to acetaldehyde formation. As expected, quantum effects are important at low temperatures.

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## 1 Introduction

The complexity of the chemical networks that take part in the formation and fragmentation processes of interstellar species depend on the physical evolution of the star-formation cycles, such as changes in density, temperature, and spectral shape and intensity of radiation.<sup>1</sup> The synthesis of interstellar species occurs in some cases on surfaces of grains, or *via* gas phase reactions, and in some other cases as a combination of these. Knowledge of the pathways that lead to the synthesis of organic

molecules in space could help in understanding if such chemistry could lead to the emergence of life on Earth.<sup>2</sup>

The search for the chemical routes leading to the formation of interstellar Complex Organic Molecules (COMs), *viz.* organic species with six or more atoms,<sup>3,4</sup> has motivated several research groups to investigate them theoretically,<sup>5–11</sup> observationally,<sup>1,12</sup> and experimentally.<sup>13–15</sup> In particular, acetaldehyde (CH<sub>3</sub>CHO) was first detected in 1973 (ref. 16) and plays a key role in the chemistry of the Interstellar Medium (ISM).<sup>17</sup> Astronomical observations toward cold and dark clouds in star-forming regions show the abundance of acetaldehyde to be approximately  $\sim 10^{-10}$  to  $10^{-9}$  with respect to the density of H<sub>2</sub>.<sup>18–20</sup> Acetaldehyde has been observed in the gas phase toward several environments such as translucent clouds,<sup>21</sup> pre-stellar cores,<sup>22</sup> the comet Hale–Bopp<sup>23</sup> but also in interstellar ices<sup>6,7,24</sup> and meteorites.<sup>25</sup>

Acetaldehyde is the simplest methyl-bearing aldehyde and constitutes a critical precursor to prebiotic molecules such as glycolaldehyde (CH<sub>2</sub>OHCHO)<sup>26</sup> and acrolein (CH<sub>2</sub>CHCHO). The latter is a crucial intermediate in the prebiotic synthesis of various amino acids<sup>27</sup> and plays an important role in astrobiology.<sup>28</sup> For these reasons, CH<sub>3</sub>CHO is one of the most studied molecules in the ISM in recent years.

So far, formation of acetaldehyde has been investigated in the gas phase,<sup>29,30</sup> on pure water ice models,<sup>31–33</sup> ice containing

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† Electronic supplementary information (ESI) available: The following files are available free of charge, COORD: ASCII files for all XYZ coordinates pertaining to I<sub>1</sub>, I<sub>2</sub>, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub>, TS1, TS2, TS3 and TS4 for possible spin states  $S = 0, 1$ . This material is available free of charge *via* the Internet at <https://pubs.acs.org/>. See <https://doi.org/10.1039/d2ra03555c>



methanol,<sup>34</sup> and on amorphous CO-rich ice cluster models.<sup>6,7,35,36</sup> Quantum chemical calculations on the formation of CH<sub>3</sub>CHO from the reaction between HCO and CH<sub>3</sub> radicals have been performed by Enrique-Romero *et al.*<sup>31</sup> The broken symmetry (BS) approach was not initially considered in their DFT calculations, and only CH<sub>4</sub> + CO can be formed on an amorphous molecular water ice cluster. In gas phase, possible spontaneous products are CH<sub>3</sub>CHO, CH<sub>4</sub> + CO, and CH<sub>3</sub>OCH depending on the initial orientation of the reagents.<sup>31</sup> The gas phase formation of CH<sub>3</sub>CHO and CH<sub>3</sub>OCH however requires a third body or spontaneous emission of a photon in order to stabilize the molecules. These conclusions have been revoked later by Enrique-Romero *et al.*,<sup>33</sup> when an unrestricted BS approach was employed. As a consequence, the authors report that in gas phase the CH<sub>3</sub>CHO and CH<sub>4</sub> + CO channels are barrierless, while CH<sub>3</sub>OCH presents a high barrier. In contrast, on an ice model represented by a single H<sub>2</sub>O molecule, H transfer from HCO to CH<sub>3</sub> to form CH<sub>4</sub> + CO presented a very high barrier, while the formation of CH<sub>3</sub>CHO was found to be barrierless, as in the gas phase. Other calculations on two model clusters comprised of 18 and 33 water molecules reported similar findings.<sup>32</sup>

Synthesis of acetaldehyde in the gas phase has been studied through several mechanisms using the KIDA<sup>37</sup> and UFA<sup>38</sup> databases.

None of these appear to yield sufficient acetaldehyde to explain its interstellar abundance and Vazart and co-workers<sup>5</sup> wrote a critical review of the gas-phase formation routes of acetaldehyde invoked in the literature. The prevailing theory of the formation of COMs relies on their chemistry at the surface of warm grains. Acetaldehyde has, however, been observed at very low temperatures, hence challenging the warm scenario.

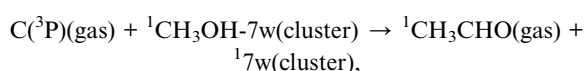
Bennett and co-workers<sup>6,7</sup> studied synthetic routes toward acetaldehyde formation inside ice mixtures of carbon monoxide and methanol condensed at 10 K from both experimental and computational points of view.

These and other laboratory experiments provide compelling evidence that acetaldehyde can easily form in interstellar ices containing carbon monoxide and methane,<sup>6,7,35</sup> methanol,<sup>34</sup> ethane (CH<sub>3</sub>CH<sub>3</sub>) or ethylene (CH<sub>2</sub>CH<sub>2</sub>),<sup>39</sup> and pure methanol ices,<sup>40</sup> or by oxidation of ethanol (CH<sub>3</sub>CH<sub>2</sub>OH)<sup>41</sup>/2-propanol (CH<sub>3</sub>CH<sub>2</sub>OHCH<sub>3</sub>)<sup>42,43</sup> when exposed to ionizing radiation.<sup>42</sup>

In this article, we focus on a solid-state chemistry formation mechanism that has been proposed in the literature.<sup>44</sup> We perform new electronic structure calculations on the energetics of this mechanism. Our main purpose is to investigate the role of the spin and calculate thermal rate constants for the rate limiting step of the proposed mechanism. This information can then be used in astrochemical modelling.

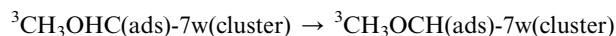
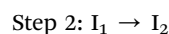
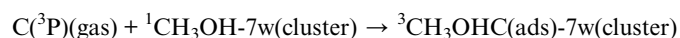
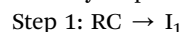
We study the formation of acetaldehyde following the Eley-Rideal mechanism where gas phase C(<sup>3</sup>P) approaches a methanol molecule which is part of a model grain also composed of 7 water molecules.

The overall reaction is:

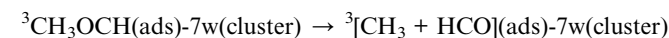
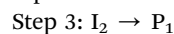


where 7w(cluster) stands for a cluster of 7 water molecules.

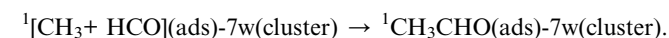
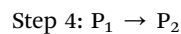
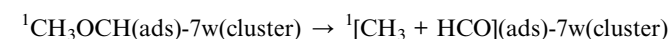
Singh *et al.*<sup>44</sup> proposed, where we below essentially use their notation, some (involving only total spin  $S = 1$ ) of the following elementary steps:



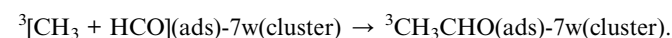
We also consider intersystem crossing and investigate formation of <sup>1</sup>CH<sub>3</sub>OCH(ads)-7w(cluster) in Step 2. Consequently, the Step 3 below has also been studied on the singlet spin potential energy surface in this paper.



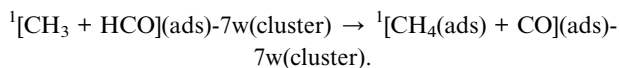
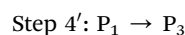
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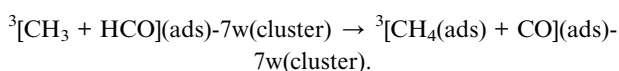
or



We will additionally comment on:



and



In Section 2 we describe the adopted computational methods for electronic structure and rate constants calculations and in Section 3 we discuss the results and their implications. Finally conclusions are given in Section 4.

## 2 Methodology

In the present work we employ density functional theory (DFT),<sup>45</sup> and CCSD(T)<sup>46</sup> to investigate acetaldehyde (Ac) formation on a model grain comprised of seven water molecules and



a single methanol molecule that substitutes the 8<sup>th</sup> water molecule of a cubic cluster.

All quantum chemical calculations have been performed with the Gaussian 16 software.<sup>47</sup>

## 2.1 Density functional theory (DFT) calculations

In our work all structures are fully optimized and the harmonic frequencies computed using DFT. Frequency calculations were performed in order to verify that all intermediates are true minima on the potential energy surface, and that all transition states exhibit a single imaginary frequency.

We use the range separated U $\omega$ B97XD hybrid meta-GGA exchange–correlation functional<sup>48</sup> with its dispersion corrections which yields satisfactory accuracy for the thermochemistry, kinetics, and non-covalent interactions. Thus, it can be used to study our model system and describes accurately the interactions that play an important role in the stability of the different fragments involved in the reaction process leading to acetaldehyde.<sup>48</sup>

The split valence triple  $\zeta$  Pople basis set 6-311++G(2d,p)<sup>49</sup> includes polarisation and diffuse functions and is able to describe van der Waals interactions inside the ice model and molecular interactions with the fragments. Further, this basis set is shown to provide near experimental accuracy for many chemical reactions.<sup>50,51</sup> We study all species in the reaction mechanism with the U $\omega$ B97XD/6-311++G(2d,p) model chemistry. Gaussian 16 automatically includes an ultrafine integration grid in the DFT calculations in order to improve the accuracy of the results. The grid greatly enhances the accuracy at reasonable additional cost.

The reaction paths are computed using the intrinsic reaction coordinate (IRC) methodology<sup>52,53</sup> to confirm the identities of the reactants and products for every transition state.

IRC calculations require initial force constants of the transition state. Then, the first and second order energy derivatives are obtained to calculate the projected harmonic vibrational frequencies along each reaction path. The Minimum Energy Paths (MEPs) for Steps 2, 3 and 4 were computed using the Page–McIver integrator with a gradient step size of 0.1  $a_0$ .

## 2.2 Coupled cluster calculations

In order to better describe the energetics, single point energy calculations were performed for all involved species using CCSD(T)<sup>46</sup> on the DFT optimized geometries.

As the calculations become time intensive for larger basis set choices, the same basis set was used as in the DFT calculations and this composite method will in the following be referred to as CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p).

## 2.3 Semi-classical theory of the rate constants

Rate constants for Step 3 (for both spin states  $S = 0, 1$ ) in the reaction mechanism, which is energetically rate limiting, are computed over the temperature range [105–2000 K] with the general polyatomic rate constant code POLYRATE version 2010-A.<sup>54</sup> Transition state theory is employed in various forms as described below.

The connectivity between a transition state and the desired reactant or product is verified by performing intrinsic reaction

coordinate calculations in both the forward and backward directions with a step size of 0.1 Bohr.

**Conventional transition state theory.** The conventional transition-state-theory rate constant,  $k_{\text{TST}}(T)$ , is given by the following expression for uni-molecular reactions:<sup>55</sup>

$$k_{\text{TST}}(T) = \sigma \frac{k_{\text{B}} T}{h} \frac{Q_{\text{elec}}^{\text{TS}} Q_{\text{rot}}^{\text{TS}}(T) Q_{\text{vib}}^{\text{TS}}(T)}{Q_{\text{elec}}^{\text{R}} Q_{\text{rot}}^{\text{R}}(T) Q_{\text{vib}}^{\text{R}}(T)} \times \exp \left[ -\frac{E_{\text{TS}} - E_{\text{reactant}}}{k_{\text{B}} T} \right], \quad (1)$$

where  $E_{\text{TS}} - E_{\text{Reactant}} = \Delta V$  is the classical barrier height,  $\sigma$  represents the symmetry number referring to reaction path degeneracy,  $h$  is Planck's constant, and  $k_{\text{B}}$  is the Boltzmann constant.  $Q^{\text{TS}}$  and  $Q^{\text{R}}$  are the transition state (TS) and reactant (R) partition functions, respectively, which can be expressed as a product of the partition functions of the internal motions (vibration, rotation), and the electronic distribution. Rotational partition functions are calculated classically within the rigid rotor harmonic oscillator approximation and the vibrational partition functions are calculated as separable quantum mechanical harmonic oscillators.  $\sigma$  is always unity in the present work.

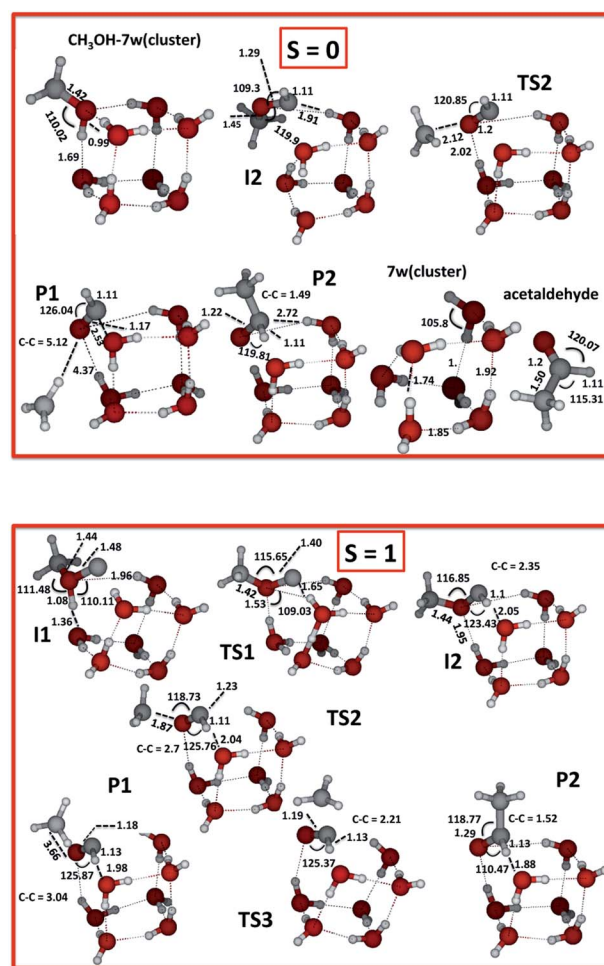


Fig. 1 Fully optimised final geometries for all reactants, and complexes computed with U $\omega$ B97XD/6-311++G(2d,p) for the two spin states  $S = 0$  and 1.



**Canonical variational transition state theory.** Canonical variational transition-state theory (CVT)<sup>56</sup> has been used to estimate the rate constants. The canonical variational, transition state theory rate constant  $k_{\text{CVT}}$  is obtained by finding the location of the minimum flux through the transition state at a given temperature.

Note that in using a free energy of activation criterion to determine the location of the variational transition state, both entropic and energetic contributions are taken into account. We may write:

$$k_{\text{CVT}}(T) = \min_s k^{\text{G}}(T, s) = k^{\text{G}}(T, s^{\star, \text{CVT}}(T)), \quad (2)$$

where

$$k^{\text{G}}(T, s) = \sigma \frac{k_{\text{B}} T}{h} \frac{Q^{\text{TS}}(T, s)}{Q^{\text{R}}(T)} \exp\left[-\frac{V_{\text{MEP}}(s)}{k_{\text{B}} T}\right]. \quad (3)$$

Here  $V_{\text{MEP}}(s)$  is the classical potential along the minimum energy path referenced to the reactant energy,  $s$  is the mass scaled reaction coordinate and  $s^{\star, \text{CVT}}$  is the location of the canonical transition state on the reaction path, *i.e.* where the flux is minimal.

$s = 0$  at the transition state, at the reactants it is a finite negative number, and for the products a finite positive number.

**Zero curvature tunneling (ZCT) method.** When the reaction path curvature can be neglected, the proper tunneling path is the MEP. For tunneling along the MEP,  $\theta(E)$  is used to describe the imaginary action integral given by

$$\theta(E) = \hbar^{-1} \int_{s_0}^{s_1} ds [2\mu [V_{\text{a}}^{\text{G}}(s) - E]]^{1/2}, \quad (4)$$

where  $V_{\text{a}}^{\text{G}}(s) = V_{\text{MEP}}(s) + \text{ZPE}(s)$ , and ZPE is the zero point energy corresponding to the frequencies orthogonal to the reaction path.

A tunnelling probability is calculated as

$$P(E) = \exp[-2\theta(E)], \quad (5)$$

which can be used to obtain a transmission coefficient  $\kappa(T)$  from,

$$\kappa(T) = \frac{\int_0^{\infty} P(E) \exp\left(-\frac{E}{k_{\text{B}} T}\right) dE}{\int_{V_{\text{a}}^{\text{G}}(s=0)}^{\infty} \exp\left(-\frac{E}{k_{\text{B}} T}\right) dE}. \quad (6)$$

This  $\kappa(T)$  multiplies the otherwise obtained thermal rate constant to give a tunnelling corrected rate constant,

$$k_{\text{ZCT}}(T) = \kappa(T) \times k_{\text{TST}}(T). \quad (7)$$

This approach is called the zero curvature tunneling (ZCT) method.<sup>57</sup>

**Small curvature tunneling (SCT) method.** Liu *et al.*<sup>56</sup> have reported that tunnelling probabilities may increase because of the so called corner-cutting effect, which is not accounted for in the ZCT method. More advanced tunneling methods are based on the inclusion of deviations between the tunneling path and the minimum energy path.<sup>58</sup>

In the small curvature tunneling method (SCT),<sup>56</sup> transmission coefficients,<sup>57,59</sup> which include effects of the reaction-path curvature, are based on the centrifugal-dominant small-curvature semi-classical adiabatic ground-state (CD-SCSAG)

**Table 1** Energies (in Hartree) for a total spin  $S = 0$  and 1 computed at U $\omega$ B97XD/6-311++G(2d,p) and CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) levels and zero point energies at U $\omega$ B97XD/6-311++G(2d,p) level for all species involved along the reaction path

Species	Energy (U $\omega$ B97XD)	ZPE (U $\omega$ B97XD)	Energy + ZPE (U $\omega$ B97XD)	Energy CCSD(T)//U $\omega$ B97XD	Energy + ZPE CCSD(T)//U $\omega$ B97XD
<b>S = 1</b>					
C( <sup>3</sup> P)	-37.840178	—	-37.840178	-37.773973	-37.773973
I <sub>1</sub>	-688.780084	0.236295	-688.543789	-687.548089	-687.311794
TS1	-688.777331	0.230375	-688.546956	-687.541491	-687.311116
I <sub>2</sub>	-688.828564	0.235519	-688.593045	-687.595794	-687.360275
TS2	-688.801766	0.230675	-688.571091	-687.569784	-687.339109
P <sub>1</sub>	-688.837208	0.227453	-688.609755	-687.609865	-687.382412
TS3	-688.834115	0.230081	-688.604034	-687.601360	-687.371279
P <sub>2</sub>	-688.862109	0.234261	-688.627848	-687.623084	-687.388823
TS4	-688.790605	0.228354	-688.562251	-687.551798	-687.323444
P <sub>3</sub>	-688.807343	0.233586	-688.573757	-687.571456	-687.337870
CH <sub>3</sub> CHO(gas)	-153.709122	0.052916	-153.656206	-153.399772	-153.346856
<b>S = 0</b>					
Ice model: CH <sub>3</sub> OH-7w	-650.894314	0.235504	-650.658810	-649.742209	-649.506705
7w(cluster)	-535.138321	0.179647	-534.958674	-534.211967	-534.032320
I <sub>2</sub>	-688.875062	0.237861	-688.637201	-687.644363	-687.406502
TS2	-688.827359	0.229755	-688.597604	-687.597604	-687.368810
P <sub>1</sub>	-688.837677	0.227578	-688.610099	-687.610245	-687.382667
P <sub>2</sub>	-688.982611	0.237554	-688.745056	-687.750202	-687.512648
P <sub>3</sub>	-688.973831	0.232680	-688.741151	-687.755034	-687.522354
CH <sub>3</sub> CHO(gas)	-153.829051	0.055686	-153.773365	-153.523343	-153.467657



approximation.<sup>56</sup> The SCT method is known to predict reasonably accurate rate constants<sup>60–62</sup> and is therefore widely used.

In the SCT method the effect of the reaction curvature is included by replacing the reduced mass  $\mu$  by an effective mass  $\mu_{\text{eff}}$ . The tunnelling probability at energy  $E$  is

$$P(E) = \frac{1}{1 + e^{-2\theta(E)}} \quad (8)$$

where  $\theta(E)$  is the imaginary action integral along the tunnelling path

$$\theta(E) = \hbar^{-1} \int_{s_0}^{s_1} ds \{2\mu_{\text{eff}} [V_a^G - E]\}^{1/2}. \quad (9)$$

$\kappa(T)$  is calculated as in eqn (4) and the thermal rate constant is tunnelling corrected in the corresponding way as done for ZCT. Details of the theory can be found in ref. 63.

### 3 Results and discussion

In this section we first report our electronic structure calculations and then the rate constants that we have obtained for the

energetically rate determining step, Step 3, on both the singlet and triplet potential energy surfaces.

#### 3.1 Electronic structure calculations

From the electronic structure calculations we computed intermediates, transition states and products as illustrated in Fig. 1 for the singlet and triplet species.

All structures are optimised at the  $U\omega B97XD/6-311++G(2d,p)$  level. Transition states correspond to the first-order saddle points characterized by single imaginary frequencies. For the triplet species these frequencies are  $758i \text{ cm}^{-1}$  for the H atom transfer in Step 2,  $762i \text{ cm}^{-1}$  for the C–O bond breakage in Step 3,  $243i \text{ cm}^{-1}$  for the C–C bond formation in Step 4, and  $1445i \text{ cm}^{-1}$  for the H abstraction in Step 4'.

As the carbon atom approaches the  $\text{CH}_3\text{OH}$ –water complex, the formation of intermediate  $I_1$  occurs without a barrier (Step 1). This is followed by hydrogen transfer from the oxygen atom of methanol to the carbon atom *via* a proton relay-mechanism involving the water molecules of the ice model through the transition state TS1, to yield a more stable intermediate  $I_2$  (Step 2). Another barrier-mediated (TS2) step generates the adsorbed radicals  $\text{CH}_3$  and  $\text{HCO}$ , *i.e.* the  $P_1$  complex (Step 3). These first three steps may occur on the triplet PES. Spin flip could however take place close to the intermediate  $I_2$  ( $S = 1$ ), thereby yielding  $I_2$  ( $S = 0$ ). This would allow the reaction to continue on the singlet PES, see more below. In Step 4 acetaldehyde adsorbed on the ice ( $P_2$ ) forms.

We have computed the possible fragments on the singlet ( $S = 0$ ) PES employing “Stable = Opt” first to ensure that we get the lowest singlet SCF solution, as we are interested in finding an SCF solution of an open shell unrestricted singlet wavefunction. For  $S = 0$ , our calculations lead to the following stationary species  $I_2$ , TS2,  $P_1$ ,  $P_2$  and  $P_3$ , as seen in Table 1. Step 3 has a transition state TS2, as can be seen in Fig. 1 and 2, and a single imaginary frequency of  $464i \text{ cm}^{-1}$ .

The energies of the fragments and their corresponding zero point energies are given in Table 1, for each spin state.

We provide in the ESI† the Cartesian coordinates for all fragments involved in the two spin states.

In Table 2 we collect the computed energetics for both total spin states,  $S = \{0,1\}$ .

In Fig. 2 we plot the relative classical and adiabatic energies of the reaction mechanism under consideration. We see that on the triplet PES, Step 2 can lead to the formation of intermediate  $I_2$  without a barrier to reaction on the  $U\omega B97XD/6-311++G(2d,p)$  vibrationally adiabatic PES while there is a small barrier of  $0.43 \text{ kcal mol}^{-1}$  using  $\text{CCSD(T)}/U\omega B97XD$ , whereas ref. 44 reports a barrier of  $5 \text{ kcal mol}^{-1}$ .

To balance the computational cost and chemical accuracy, the MEP energies were refined by performing  $\text{CCSD(T)}/U\omega B97XD/6-311++G(2d,p)$  single-point energy calculations on the  $U\omega B97XD/6-311++G(2d,p)$  IRC optimized stationary points. The comparison between the MEP energies obtained with the two levels of theory for Steps 2 & 3 can be seen in Fig. 3 and 4.

In Fig. 5 we plot the potential energy, ZPE, and vibrationally adiabatic ground state energy  $V_a^G$  along the minimum energy

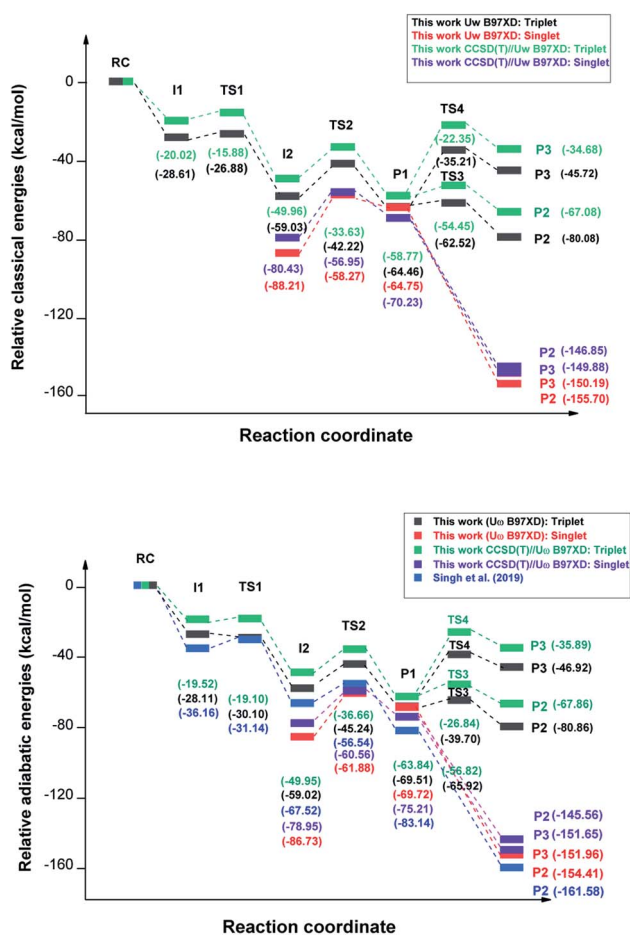


Fig. 2 Schematic potential energy surfaces for the complete reaction mechanism computed with  $U\omega B97XD/6-311++G(2d,p)$  and  $\text{CCSD(T)}/U\omega B97XD$ . Relative classical (top) and adiabatic (bottom) energies are compared to those from ref. 44 (blue lines). We plot our calculated values for the two spin states  $S = 0$  (red and purple lines) and  $S = 1$  (black and green lines).



**Table 2** Energetics of the different steps in the reaction mechanism using U $\omega$ B97XD, and CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) level in kcal mol<sup>-1</sup> for  $S = 0$  and 1. Classical barrier height ( $\Delta V$ ), the vibrational adiabatic ground state barrier height ( $\Delta V_a^G$ ), classical ergicity ( $\Delta E$ ) and vibrational adiabatic ergicity ( $\Delta E_a$ ) are shown<sup>a</sup>

Method	Label	U $\omega$ B97XD				CCSD(T)//U $\omega$ B97XD			
		$\Delta V$	$\Delta V_a^G$	$\Delta E$	$\Delta E_a$	$\Delta V$	$\Delta V_a^G$	$\Delta E$	$\Delta E_a$
<b>S = 1</b>									
RC $\rightarrow$ I <sub>1</sub>	Step 1	—	—	-28.61	-28.11	—	—	-20.02	-19.53
I <sub>1</sub> $\rightarrow$ I <sub>2</sub>	Step 2	1.727	-1.987	-30.42	-30.91	4.14	0.43	-29.93	-30.42
I <sub>2</sub> $\rightarrow$ P <sub>1</sub>	Step 3	16.82	13.78	-5.42	-10.49	16.32	13.28	-8.83	-13.89
P <sub>1</sub> $\rightarrow$ P <sub>2</sub>	Step 4	1.94	3.59	-15.63	-11.35	5.34	6.98	-8.29	-4.02
P <sub>1</sub> $\rightarrow$ P <sub>3</sub>	Step 4'	29.24	29.81	18.74	22.59	36.44	37.00	24.10	27.95
<b>S = 0</b>									
I <sub>2</sub> $\rightarrow$ P <sub>1</sub>	Step 3	29.93	24.85	23.46	17.01	28.73	23.55	21.41	14.96
P <sub>1</sub> $\rightarrow$ I <sub>2</sub>	Step 3'	6.47	7.84	-23.46	-17.01	13.28	14.65	-21.41	-14.96
P <sub>1</sub> $\rightarrow$ P <sub>2</sub>	Step 4	—	—	-90.95	-84.69	—	—	-76.62	-70.36
P <sub>1</sub> $\rightarrow$ P <sub>3</sub>	Step 4'	—	—	-85.44	-82.24	—	—	-79.65	-76.45
P <sub>2</sub> $\rightarrow$ Ac(gas) + 7w(cluster)		—	—	9.56	8.17	—	—	9.34	7.95

<sup>a</sup> — indicates barrierless.

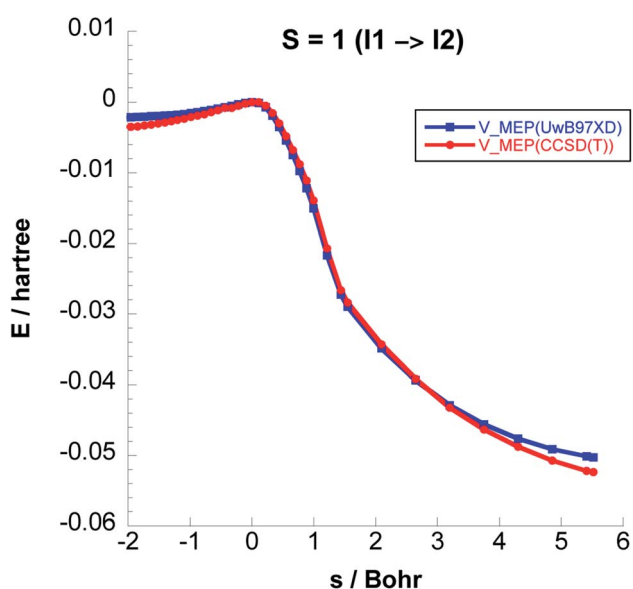
path for Step 2. The ZPE variation with respect to the reaction coordinate  $s$  exhibits a dip around the transition state, which results in that the 4.14 kcal mol<sup>-1</sup> classical barrier is reduced to 0.43 kcal mol<sup>-1</sup>.

Fig. 6 shows the reaction path pertaining to Step 3 on the triplet surface, *i.e.* the energetically rate determining step. The adiabatic barrier height is 13.28 kcal mol<sup>-1</sup> for this step, which is exothermic. Formation of adsorbed acetaldehyde (Ac) through Step 4 is exothermic by -8.29 kcal mol<sup>-1</sup> with a moderate vibrationally adiabatic barrier height of 6.98 kcal mol<sup>-1</sup>. In Fig. 7 we plot, for Step 4 the U $\omega$ B97XD/6-

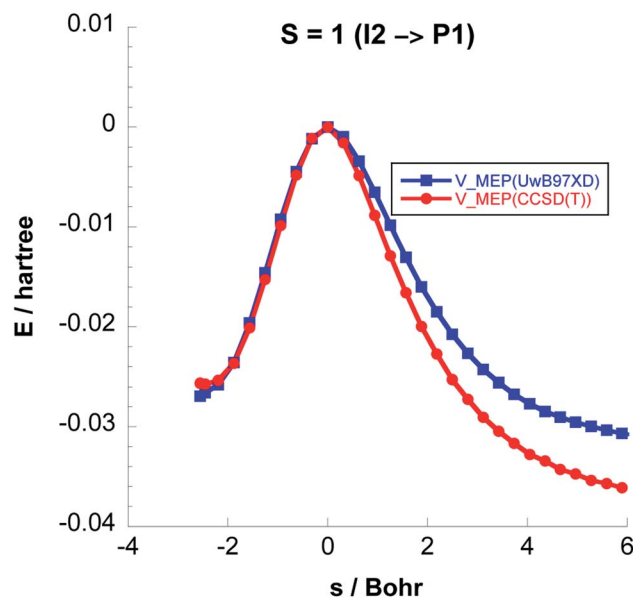
311++G(2d,p)  $V_{\text{MEP}}(s)$ ,  $V_a^G(s)$  and ZPE( $s$ ) where we clearly see how the variation in ZPE results in an increase of the adiabatic barrier.

The I<sub>2</sub> singlet state has a noticeably lower energy (see Table 1) than the triplet state. We have therefore investigated if a spin flip could happen such that I<sub>2</sub> may form in its singlet state.

We have computed the downhill reaction path starting from the triplet I<sub>2</sub> geometry but with a total spin  $S = 0$ . We also computed the single point energies for each geometry of this path with total spin  $S = 1$ . The energies are shown in Fig. 8. The crossing point between the two states is only about 3 kcal mol<sup>-1</sup>



**Fig. 3** Comparison between the classical potential energies  $V_{\text{MEP}}$ , computed with CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) and U $\omega$ B97XD/6-311++G(2d,p) levels, for Step 2 on the  $S = 1$  PES.



**Fig. 4** Comparison between the classical potential energies  $V_{\text{MEP}}$ , computed with CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) and U $\omega$ B97XD/6-311++G(2d,p) levels, for Step 3 on the  $S = 1$  PES.



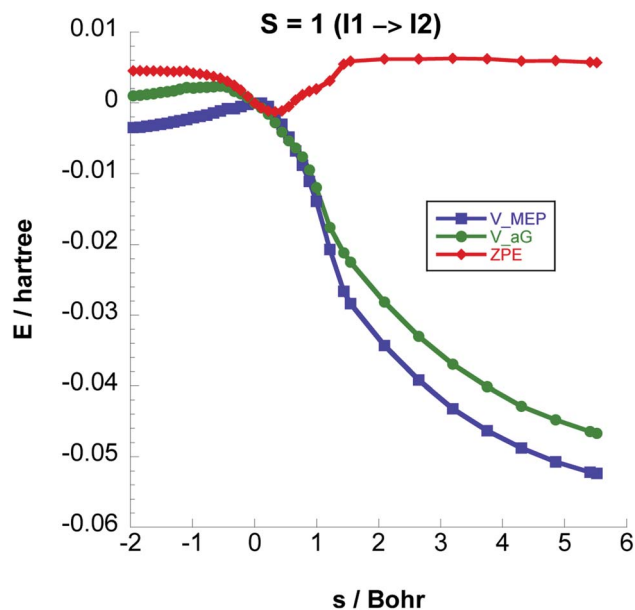


Fig. 5 Classical potential energies  $V_{\text{MEP}}$ , ground-state vibrational adiabatic potential energy curves ( $V_{\text{a}}^{\text{G}}$ ), and ZPE as functions of  $s$  (Bohr) at the CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) level, for Step 2 at a total spin  $S = 1$ .

above the energy of the triplet  $I_2$  geometry and is thus energetically easily accessible considering the energy released in coming from  $I_1$ . The point on the IRC where the energies of triplet and singlet states are the same, indicates a possible intersystem crossing geometry such that  $I_2$  can form as a singlet.

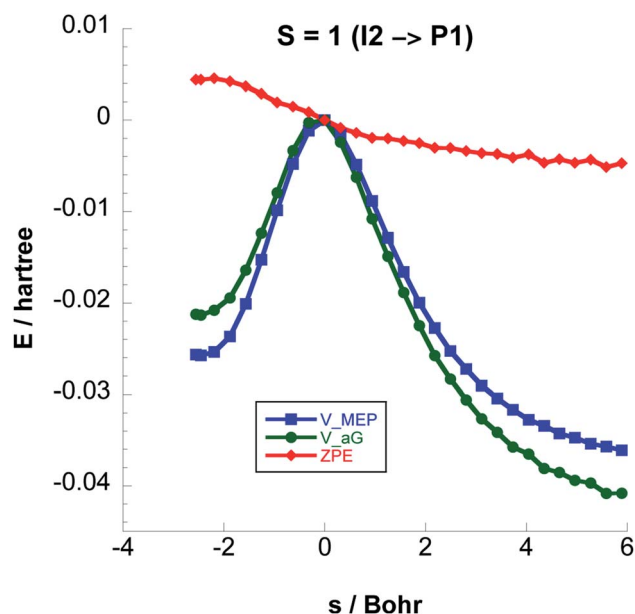


Fig. 6 Classical potential energies  $V_{\text{MEP}}$ , ground-state vibrational adiabatic potential energy curves ( $V_{\text{a}}^{\text{G}}$ ), and ZPE as functions of  $s$  (Bohr) at the CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) level, for Step 3 on the  $S = 1$  PES.

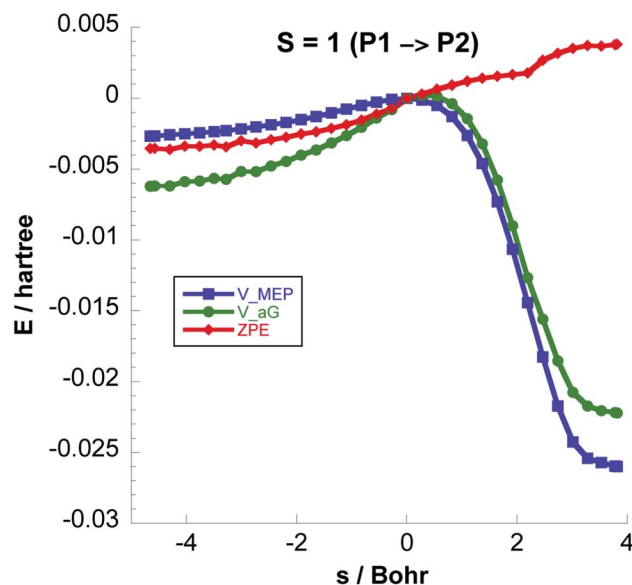


Fig. 7 Classical potential energies  $V_{\text{MEP}}$ , ground-state vibrational adiabatic potential energy curves ( $V_{\text{a}}^{\text{G}}$ ), and ZPE of 3N-6 vibrational modes as functions of  $s$  (Bohr) at the U $\omega$ B97XD/6-311++G(2d,p) level, for Step 4 at a total spin  $S = 1$ .

As a result of a spin flip close to the  $I_2$  intermediate, the next step in order to form acetaldehyde would be  $I_2$  (singlet)  $\rightarrow$   $P_1$  (singlet) instead of  $I_2$  (triplet)  $\rightarrow$   $P_1$  (triplet). In Fig. 9 we plot the classical potential energies  $V_{\text{MEP}}$  from U $\omega$ B97XD and CCSD(T)//U $\omega$ B97XD, and also the ZPE for Step 3. The adiabatic barrier height for this step is 23.55 kcal mol $^{-1}$  at the CCSD(T)//U $\omega$ B97XD level.

The following step to form adsorbed acetaldehyde (step 4) is exoergic by 70.36 kcal mol $^{-1}$ . Desorption of acetaldehyde into

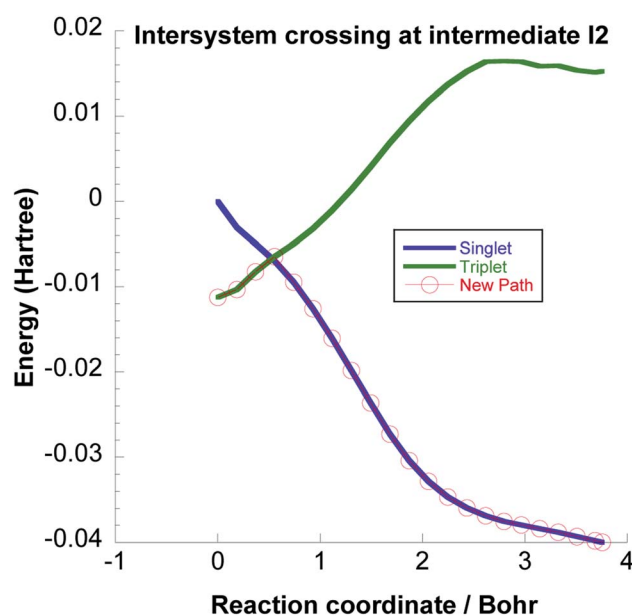


Fig. 8 Intersystem crossing between the triplet and singlet potential energy surfaces at the intermediate  $I_2$ .



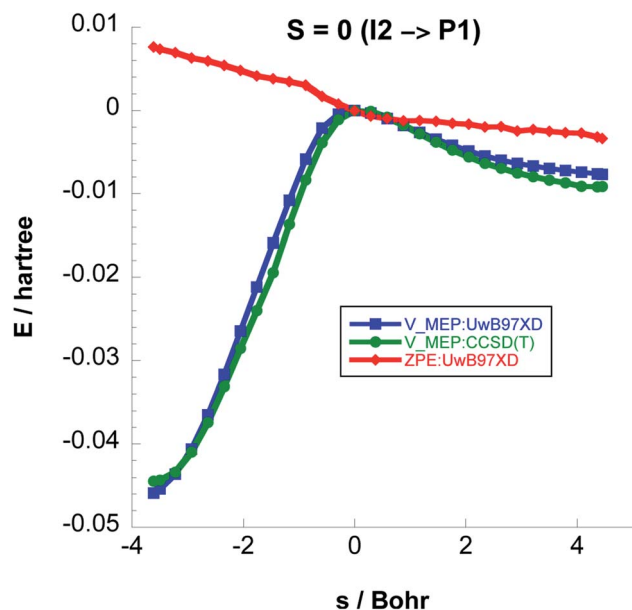


Fig. 9 Classical potential energies  $V_{\text{MEP}}$ , at the  $U\omega\text{B97XD}/6\text{-}311++\text{G}(2\text{d},\text{p})$  and  $\text{CCSD}(\text{T})//U\omega\text{B97XD}/6\text{-}311++\text{G}(2\text{d},\text{p})$  levels of theory, with ZPE as functions of  $s$  (Bohr) for Step 3 on the  $S = 0$  PES.

the gas phase is endoergic by only  $7.95 \text{ kcal mol}^{-1}$ , suggesting that the large exoergic of step 4 would lead to fast desorption.

If there is no spin flip close to  $I_2$ ,  $P_1$  would form in the triplet state. Again, the singlet  $P_1$  is lower in energy and we have investigated if a spin flip could occur also here, see Fig. 10, which is energetically quite plausible. Thereafter the reaction would proceed on the singlet surface to form adsorbed acetaldehyde which is likely to easily desorb as discussed just above.

For  $S = 0$  the  $P_1 \rightarrow P_2$  and  $P_1 \rightarrow P_3$  reactions are downhill with exoergicities of  $-70.36$  and  $-76.45 \text{ kcal mol}^{-1}$  respectively.

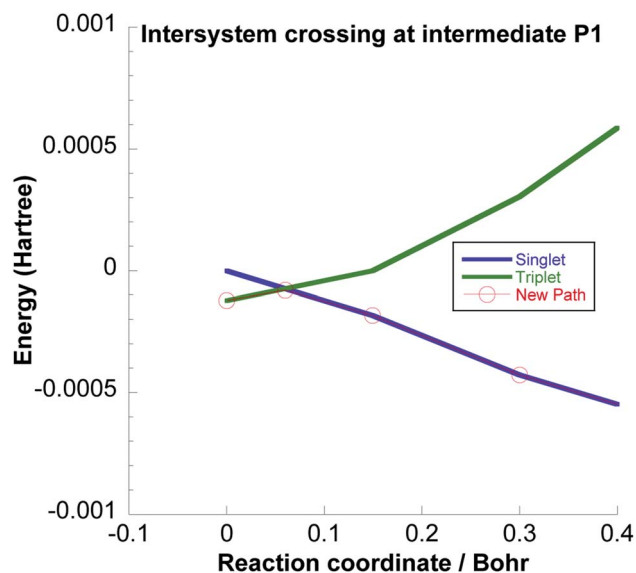


Fig. 10 Intersystem crossing between the triplet and singlet potential energy surfaces at the intermediate  $P_1$ .

Table 3 TST, CVT, CVT/ZCT, and CVT/SCT, rate constants in  $(\text{s}^{-1})$  for a total spin  $S = 1$ , for Step 3 ( $I_2 \rightarrow P_1$ ) computed at  $\text{CCSD}(\text{T})//U\omega\text{B97XD}/6\text{-}311++\text{G}(2\text{d},\text{p})$  level

$T$ (K)	TST	CVT	CVT/ZCT	CVT/SCT
105	$1.19 \times 10^{-15}$	$5.28 \times 10^{-16}$	$2.49 \times 10^{-6}$	$1.19 \times 10^{-5}$
120	$4.0 \times 10^{-12}$	$1.78 \times 10^{-12}$	$6.94 \times 10^{-6}$	$2.77 \times 10^{-5}$
150	$3.64 \times 10^{-7}$	$1.61 \times 10^{-7}$	$1.64 \times 10^{-4}$	$3.73 \times 10^{-4}$
200	$3.63 \times 10^{-2}$	$1.55 \times 10^{-2}$	$1.79 \times 10^{-1}$	$2.20 \times 10^{-1}$
300	$4.33 \times 10^3$	$1.69 \times 10^3$	$3.32 \times 10^3$	$3.47 \times 10^3$
400	$1.71 \times 10^6$	$6.01 \times 10^5$	$7.35 \times 10^5$	$7.51 \times 10^5$
500	$6.61 \times 10^7$	$2.11 \times 10^7$	$2.14 \times 10^7$	$2.17 \times 10^7$
600	$7.89 \times 10^8$	$2.33 \times 10^8$	$2.16 \times 10^8$	$2.18 \times 10^8$
700	$4.76 \times 10^9$	$1.32 \times 10^9$	$1.16 \times 10^9$	$1.17 \times 10^9$
800	$1.86 \times 10^{10}$	$4.86 \times 10^9$	$4.13 \times 10^9$	$4.15 \times 10^9$
900	$5.41 \times 10^{10}$	$1.35 \times 10^{10}$	$1.12 \times 10^{10}$	$1.12 \times 10^{10}$
1000	$1.28 \times 10^{11}$	$3.07 \times 10^{10}$	$2.48 \times 10^{10}$	$2.48 \times 10^{10}$
1200	$4.72 \times 10^{11}$	$1.04 \times 10^{11}$	$7.58 \times 10^{10}$	$7.59 \times 10^{10}$
1400	$1.21 \times 10^{12}$	$2.44 \times 10^{11}$	$1.62 \times 10^{11}$	$1.62 \times 10^{11}$
1600	$2.46 \times 10^{12}$	$4.55 \times 10^{11}$	$2.80 \times 10^{11}$	$2.81 \times 10^{11}$
1800	$4.27 \times 10^{12}$	$7.29 \times 10^{11}$	$4.35 \times 10^{11}$	$4.35 \times 10^{11}$
2000	$6.67 \times 10^{12}$	$1.06 \times 10^{12}$	$6.29 \times 10^{11}$	$6.29 \times 10^{11}$

For the reactions on the triplet PES, only one unpaired electron (on the  $\text{CH}_3$  radical) is involved in either the C–C bond formation (to form  $P_2$ ) or the H-transfer (to form  $\text{CH}_4$ ), while the other unpaired electron (on HCO-wat radical) stays uninvolved. This is obviously different than the processes on the singlet PES where the two unpaired electrons have opposite spins and they either recombine without barrier for the (C–C) bond formation or transfer an H atom without barrier to lead to two closed shell species. For these reasons on the singlet potential energy surface  $P_1 \rightarrow P_2$  (Step 4) and  $P_1 \rightarrow P_3$  (Step 4') are barrierless as can be seen in Fig. 2. Formation of adsorbed  $\text{CO} + \text{CH}_4$  products ( $P_3$ ) on the  $S = 1$  PES has a barrier of  $37 \text{ kcal mol}^{-1}$  as can be seen in Table 2.

Table 4 TST, CVT, CVT/ZCT, and CVT/SCT, rate constants in  $(\text{s}^{-1})$  for a total spin  $S = 0$ , for Step 3 ( $I_2 \rightarrow P_1$ ) computed at  $\text{CCSD}(\text{T})//U\omega\text{B97XD}/6\text{-}311++\text{G}(2\text{d},\text{p})$  level

$T$ (K)	TST	CVT	CVT/ZCT	CVT/SCT
107	$2.41 \times 10^{-34}$	$1.13 \times 10^{-34}$	$3.32 \times 10^{-32}$	$1.02 \times 10^{-31}$
120	$3.34 \times 10^{-29}$	$1.55 \times 10^{-29}$	$3.04 \times 10^{-28}$	$4.81 \times 10^{-28}$
150	$1.06 \times 10^{-20}$	$4.73 \times 10^{-21}$	$2.07 \times 10^{-20}$	$2.23 \times 10^{-20}$
200	$3.95 \times 10^{-12}$	$1.63 \times 10^{-12}$	$3.07 \times 10^{-12}$	$3.16 \times 10^{-12}$
300	$2.09 \times 10^{-3}$	$7.11 \times 10^{-4}$	$7.60 \times 10^{-4}$	$7.67 \times 10^{-4}$
400	62.3	17.8	15.2	15.2
500	$3.48 \times 10^4$	$8.44 \times 10^3$	$6.06 \times 10^3$	$6.07 \times 10^3$
600	$2.56 \times 10^6$	$5.22 \times 10^5$	$3.15 \times 10^5$	$3.16 \times 10^5$
700	$5.76 \times 10^7$	$9.93 \times 10^6$	$5.22 \times 10^6$	$5.23 \times 10^6$
800	$6.12 \times 10^8$	$8.78 \times 10^7$	$3.35 \times 10^7$	$3.35 \times 10^7$
900	$3.91 \times 10^9$	$4.64 \times 10^8$	$1.67 \times 10^8$	$1.67 \times 10^8$
1000	$1.75 \times 10^{10}$	$1.74 \times 10^9$	$6.12 \times 10^8$	$6.13 \times 10^8$
1200	$1.68 \times 10^{11}$	$1.23 \times 10^{10}$	$4.22 \times 10^9$	$4.23 \times 10^9$
1400	$8.54 \times 10^{11}$	$4.87 \times 10^{10}$	$1.73 \times 10^{10}$	$1.73 \times 10^{10}$
1600	$2.91 \times 10^{12}$	$1.35 \times 10^{11}$	$5.13 \times 10^{10}$	$5.13 \times 10^{10}$
1800	$7.60 \times 10^{12}$	$2.98 \times 10^{11}$	$1.19 \times 10^{11}$	$1.19 \times 10^{11}$
2000	$1.64 \times 10^{13}$	$5.59 \times 10^{11}$	$2.35 \times 10^{11}$	$2.35 \times 10^{11}$



Table 5  $k^{\text{CVT/SCT}} : k^{\text{CVT/ZCT}}$ ,  $k^{\text{TST}} : k^{\text{CVT}}$ , and  $k^{\text{CVT/SCT}} : k^{\text{CVT}}$  ratios for a total spin  $S = 1$ , for Step 3 ( $I_2 \rightarrow P_1$ ) computed at CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) level

$T$ (K)	$k^{\text{CVT/SCT}} : k^{\text{CVT/ZCT}}$	$k^{\text{TST}} : k^{\text{CVT}}$	$k^{\text{CVT/SCT}} : k^{\text{CVT}}$
105	4.7791	2.2538	$2.2538 \times 10^{10}$
300	1.0452	2.5621	2.0533
500	1.0140	3.1327	1.0284
800	1.0048	3.8272	0.85391
1000	1.0	4.1694	0.80782
1500	1.0	5.1765	0.64118
2000	1.0	6.2925	0.59340

### 3.2 Rate constants

In this section we report our calculated rate constants for the energetically rate determining step on both the singlet and triplet potential energy surfaces. The thermal rate constants are evaluated by means of canonical variational transition-state theory, *i.e.* CVT, in which the flux is minimized for a canonical ensemble.<sup>64</sup> ZCT and SCT tunneling corrections have been computed for the temperature range 105–2000 K where the fully optimised structures, energies, gradients, and force constants of points along the MEP are provided as inputs. Tables 3 and 4 summarize the TST, CVT, CVT/ZCT, and CVT/SCT, rate constants computed at various temperatures.

The variational effect is defined as the ratio between the TST and CVT rate constants, and the tunneling effect is the ratio between the (CVT/ZCT, CVT/SCT) and CVT rate constants. The ratio between CVT/ZCT and CVT/SCT gives information about the reaction path curvature in the vicinity of the transition state. As such, for Step 3, the CVT/SCT rate constants are predicted to be consistently larger than the CVT/ZCT ones at the same temperature.

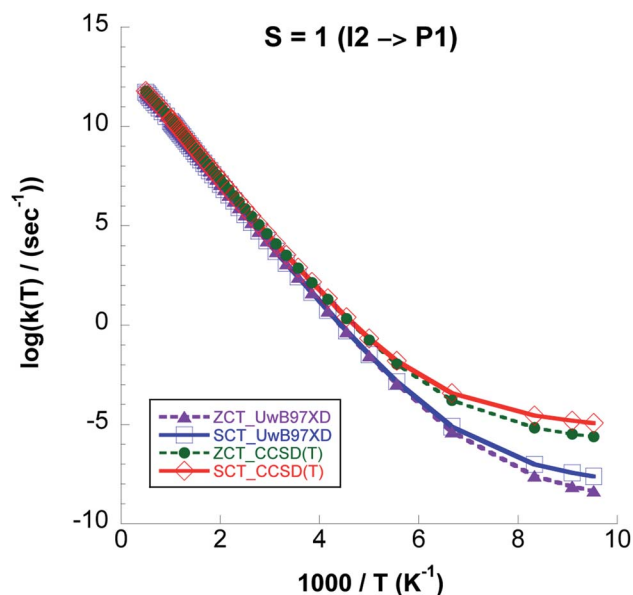


Fig. 12 Logarithm of  $k(\text{CVT/ZCT})$  and  $k(\text{CVT/SCT})$  rate constants, computed with CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) and U $\omega$ B97XD/6-311++G(2d,p) levels, for Step 3 on the  $S = 1$  PES.

In Table 5, we give the calculated ratios of  $k^{\text{CVT/SCT}} : k^{\text{CVT/ZCT}}$ ,  $k^{\text{TST}} : k^{\text{CVT}}$ , and  $k^{\text{CVT/SCT}} : k^{\text{CVT}}$  at some selected temperatures, indicating the importance of the small-curvature, variational and tunneling effects.

Table 5 and Fig. 11 show that tunneling totally dominates at the lowest temperature, but quickly becomes insignificant with increasing temperature, such that reflection by the barrier becomes more important. We also see that the variational effects affect the rate constant, particularly at high temperature.

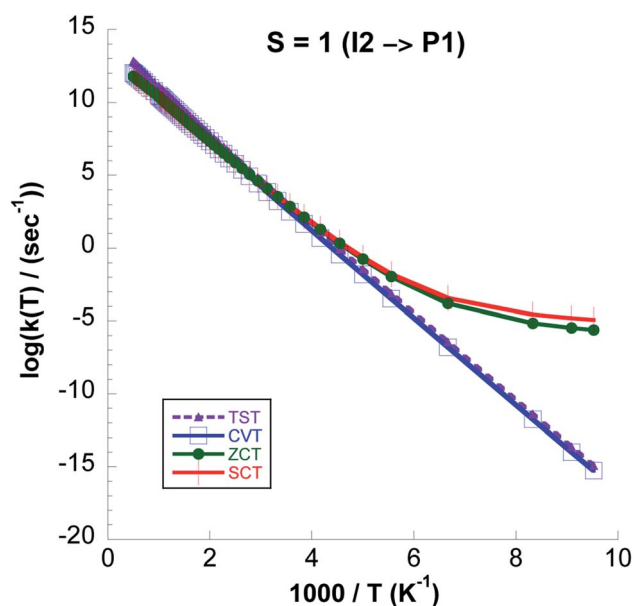


Fig. 11 Logarithmic representation of the  $k(\text{TST})$ ,  $k(\text{CVT})$ ,  $k(\text{CVT/ZCT})$  and  $k(\text{CVT/SCT})$  rate constants computed at the CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) level for the  $I_2 \rightarrow P_1$  reaction versus  $1000/T$  for  $S = 1$ .

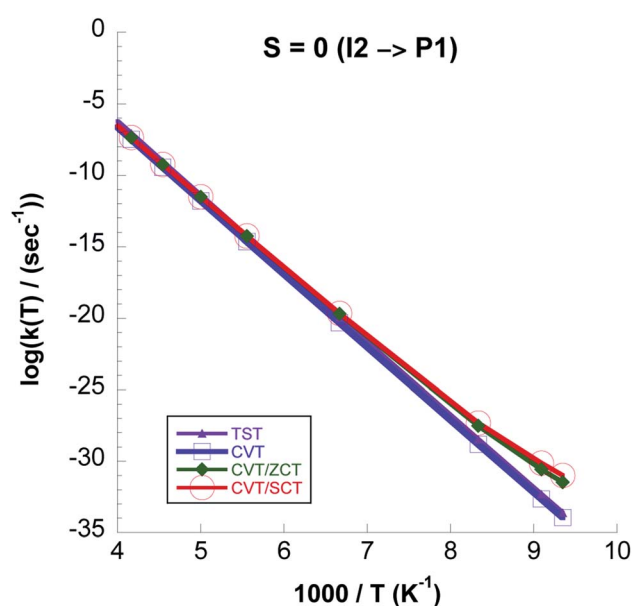


Fig. 13 Logarithmic representation of the  $k(\text{TST})$ ,  $k(\text{CVT})$ ,  $k(\text{CVT/ZCT})$  and  $k(\text{CVT/SCT})$  rate constants computed at the CCSD(T)//U $\omega$ B97XD/6-311++G(2d,p) level for the  $I_2 \rightarrow P_1$  reaction versus  $1000/T$  for  $S = 0$ .



From Fig. 12 where we compare (CVT/ZCT) and (CVT/SCT) rate constants computed with  $U\omega B97XD/6-311++G(2d,p)$  and  $CCSD(T)//U\omega B97XD/6-311++G(2d,p)$  on the triplet surface we see that the latter model chemistry predicts 4 orders of magnitude higher rate values due to the lower barrier. On the singlet surface, the shape of the reaction path in Fig. 9 shows a broad barrier resulting in only  $\sim 3$  orders of magnitude difference between the CVT/SCT rates and those from purely classical TST at the lowest temperature.

In Fig. 13 we plot rate constants computed for the  $I_2 \rightarrow P_1$  step and total spin  $S = 0$ . We see that quantum tunneling is only important at temperatures lower than  $\sim 130$  K. This is also seen from the  $k^{CVT/SCT} : k^{CVT}$  ratio in Table 6. Except for the highest temperatures the CVT/SCT rate constants on the  $S = 0$  surface are much lower than those on the  $S = 1$  PES. From Fig. 14 it is seen that for the whole temperature range  $CCSD(T)//U\omega B97XD/6-311++G(2d,p)$  rate constants are higher than those computed with  $U\omega B97XD/6-311++G(2d,p)$ .

Table 6  $k^{CVT/SCT} : k^{CVT/ZCT}$ ,  $k^{TST} : k^{CVT}$ , and  $k^{CVT/SCT} : k^{CVT}$  ratios for a total spin  $S = 0$ , for Step 3 ( $I_2 \rightarrow P_1$ ) computed at  $CCSD(T)//U\omega B97XD/6-311++G(2d,p)$  level

$T$ (K)	$k^{CVT/SCT} : k^{CVT/ZCT}$	$k^{TST} : k^{CVT}$	$k^{CVT/SCT} : k^{CVT}$
106	3.1337	2.1298	$1.2840 \times 10^3$
300	1.0081	2.9478	1.0783
500	1.0020	4.1292	0.71910
800	1.0019	6.9857	0.38286
1000	1.0018	10.0	0.35188
1500	1.0	19.512	0.36856
2000	1.0	29.408	0.42130

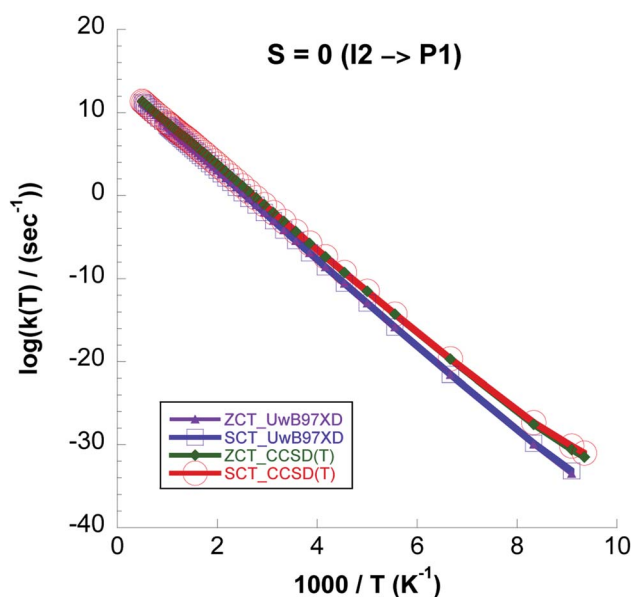


Fig. 14 Comparison between the logarithmic representation of the  $k(CVT/ZCT)$  and  $k(CVT/SCT)$  rate constants computed with the  $U\omega B97XD/6-311++G(2d,p)$  and the  $CCSD(T)//U\omega B97XD/6-311++G(2d,p)$  level of theory for the  $I_2 \rightarrow P_1$  reaction versus  $1000/T$  for  $S = 0$ .

The present work aims to improve the understanding of the reaction mechanisms and kinetics of radical–radical addition on a methanol–water ice model.

The data we provide is of a major interest in regard to astrochemical models. Other molecular species in the ice composition can also be tested in the future, in order to investigate to what extent acetaldehyde formation paths can differ and how the composition of species influences the reaction mechanisms that may change in specific astronomical sources such as cold or hot molecular cores, and star forming regions.

## 4 Conclusions

We have investigated an Eley-Rideal-type mechanism where  $C(^3P)$  reacts with  $CH_3OH$  adsorbed on a water cluster. We consider the reaction mechanism on the triplet and the singlet surfaces and discuss two possible intersystem crossings. The reaction begins on the triplet surface and is downhill. It may spin flip close to the first intermediate, *i.e.* between TS1 and TS2. If that happens the reaction continues on the singlet PES, where however the energetically rate limiting step,  $I_2$  to  $P_1$ , is much slower than on the triplet surface at interstellar temperatures.

The reaction may on the other hand remain on the triplet surface, pass TS2 and close to  $P_1$  cross to the singlet surface. From  $P_1$  to  $P_2$ , *i.e.* to form adsorbed acetaldehyde, the reaction is barrierless and exoergic by  $70.36 \text{ kcal mol}^{-1}$ . Desorption of the acetaldehyde only requires  $8 \text{ kcal mol}^{-1}$  and is thus likely to happen fast given the large exoergic of the previous step. This thus appears to be a plausible route to acetaldehyde formation in the gas phase.

We use transition state theory, with tunnelling corrections, to obtain the thermal rate constants for the energetically rate determining step of the reaction mechanism. In this step adsorbed  $CH_3OCH$  breaks up to form adsorbed  $CH_3$  and  $HCO$  (on both the triplet and singlet surfaces).

Specifically, variational transition state theory calculations with zero curvature and small tunneling corrections are employed to find thermal rate constants over the temperature range 105–2000 K, relevant to a set of astrophysical environments.

The variational effect is found to be important and have a dominating effect on the obtained rate constants except at the lowest temperature. Tunneling totally dominates the rate constant at the lowest temperature but decreases quickly as the temperature increases. In fact reflection by the barrier clearly dominates over tunneling at the higher temperatures.

We also notice that the zero curvature tunneling correction works just as well as the small curvature correction except at the lowest temperature reported in Tables 5 and 6.

This study may serve as a useful investigation for further model variants to be explored computationally, and to suggest possible constraints on new experimental setups relevant to ice models to gain new impetus in the understanding of COM formation on icy mantles in general.



## Conflicts of interest

There are no conflicts to declare.

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