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# The $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}_2 \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})/\text{O}(^3\text{P})$ reaction: thermal and vibrational relaxation rates from 15 K to 20 000 K†

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Thermal rates for the  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})/\text{O}(^3\text{P})$  reaction are investigated over a wide temperature range based on quasi classical trajectory (QCT) simulations on 3-dimensional, reactive potential energy surfaces (PESs) for the  $^1\text{A}'$ ,  $(2)^1\text{A}'$ ,  $^1\text{A}''$ ,  $^3\text{A}'$  and  $^3\text{A}''$  states. These five states are the energetically low-lying states of  $\text{CO}_2$  and their PESs are computed at the MRCISD+Q/aug-cc-pVTZ level of theory using a state-average CASSCF reference wave function. Analysis of the different electronic states for the  $\text{CO}_2 \rightarrow \text{CO} + \text{O}$  dissociation channel rationalizes the topography of this region of the PESs. The forward rates from QCT simulations match measurements between 15 K and 295 K whereas the equilibrium constant determined from the forward and reverse rates is consistent with that derived from statistical mechanics at high temperature. Vibrational relaxation,  $\text{O} + \text{CO}(\nu = 1,2) \rightarrow \text{O} + \text{CO}(\nu = 0)$ , is found to involve both, non-reactive and reactive processes. The contact time required for vibrational relaxation to take place is  $\tau \geq 150$  fs for non-reacting and  $\tau \geq 330$  fs for reacting (oxygen atom exchange) trajectories and the two processes are shown to probe different parts of the global potential energy surface. In agreement with experiments, low collision energy reactions for the  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-, \nu = 0) \rightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})$  lead to  $\text{CO}(^1\Sigma^+, \nu' = 17)$  with an onset at  $E_c \sim 0.15$  eV, dominated by the  $^1\text{A}'$  surface with contributions from the  $^3\text{A}'$  surface. Finally, the barrier for the  $\text{CO}_\text{A}(^1\Sigma^+) + \text{O}_\text{B}(^3\text{P}) \rightarrow \text{CO}_\text{B}(^1\Sigma^+) + \text{O}_\text{A}(^3\text{P})$  atom exchange reaction on the  $^3\text{A}'$  PES yields a barrier of  $\sim 7$  kcal mol<sup>-1</sup> (0.300 eV), consistent with an experimentally reported value of 6.9 kcal mol<sup>-1</sup> (0.299 eV).

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## Introduction

Reactions involving carbon and oxygen atoms play important roles in combustion, hypersonic flow, and planetary atmospheres.<sup>1</sup> Among those, the thermal rates for the  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$ ,  $\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+)$ , and  $\text{O}(^1\text{D}) + \text{CO}(^1\Sigma^+)$  reactions going through various electronic states of  $\text{CO}_2$  (see Fig. 1) are particularly relevant. Similarly, the vibrational deactivation of  $\text{CO}(^1\Sigma^+)$  through collisions with  $\text{O}(^3\text{P})$  is a relevant pathway for relaxation and redistribution of energy in nonequilibrium flow.<sup>2</sup>

Several independent studies have determined thermal rates for the forward  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$  reaction.<sup>3–5</sup> Using the CRESU

(Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique<sup>5</sup> the thermal rate from experiments between 15 and 295 K was measured. At 298 K the rate was  $4.8 \pm 0.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> which is within a factor of two to three of other, previous experiments.<sup>3,4,6,7</sup> In all three laval nozzle experiments it was found that the rate increases with decreasing temperature between 15 and 295 K.<sup>5,8,9</sup> The product detection techniques included vacuum ultraviolet laser-induced fluorescence,<sup>5,9</sup> and chemiluminescence.<sup>8</sup>

Shock tube experiments of the  $\text{C} + \text{O}_2$  reactions were also carried out at higher temperatures (from 1500 to 4200 K) and reported a rate of  $k_\text{f}(T) = 1.2 \times 10^{14} \exp(-2010 \text{ K}/T)$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (corresponding to  $1.9 \times 10^{-10} \exp(-2010 \text{ K}/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) with an overall uncertainty of  $\pm 50\%$  and a standard deviation for the activation energy of  $\pm 15\%$  and  $\pm 13\%$ , respectively.<sup>10</sup> Yet earlier emission spectra in a discharge flow found that the  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$  reaction generates CO in high vibrationally excited states (up to  $\nu' = 17$ ) and that the transition state has the configuration COO rather than OCO.<sup>11</sup> Such a COO intermediate was also proposed from the interpretation of the  $\text{C} + \text{O}_2$  reaction<sup>12</sup> and has been described in multiconfiguration SCF calculations.<sup>13</sup>

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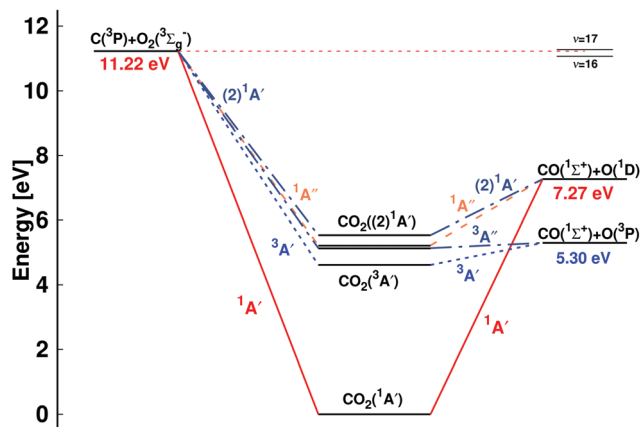
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**Fig. 1** Energy level diagram for the  $\text{C} + \text{O}_2 \leftrightarrow \text{CO} + \text{O}$  reaction:  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^3\text{P})$  and  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})$ . The energies of the dissociating species are reported: the  $\text{O}(^1\text{D})/\text{O}(^3\text{P})$  separation is 1.97 eV, consistent with experiment, and the total energies for  $\text{CO}_2$  are  $^1\text{A}'$  ( $^1\Sigma_g$  in  $D_{\infty h}$ ) (0 eV),  $^3\text{A}'$  (4.62 eV),  $^3\text{A}''$  (5.14 eV),  $^1\text{A}''$  (5.22 eV), and  $(2)^1\text{A}'$  (5.53 eV). The relative positions of the  $\text{CO}(\nu = 16) + \text{O}(^1\text{D})$  and  $\text{CO}(\nu = 17) + \text{O}(^1\text{D})$  asymptotes, relevant for discussing the low energy collision  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})$  reaction,<sup>34</sup> are indicated on the right hand side. The correlation of the  $(2)^1\text{A}'$  state of  $\text{CO}_2$  based on state-averaged SA-CASSCF calculations given in Fig. S1 (ESI<sup>†</sup>) with the reactant and product state is consistent with earlier work<sup>8</sup> but differs from others.<sup>13</sup>

Also, no evidence was found that the  $\text{C} + \text{O}_2$  reaction passes through the region where the quenching of  $\text{O}(^1\text{D})$  to  $\text{O}(^3\text{P})$  by  $\text{CO}$  occurs as a non-adiabatic process, as had been proposed earlier.<sup>14,15</sup>

For the reverse reactions,  $\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+)$ , and  $\text{O}(^1\text{D}) + \text{CO}(^1\Sigma^+)$  leading to  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$ , the onset for the rates  $k_r(T)$  to form  $\text{C} + \text{O}_2$  is expected to occur at considerably higher temperature than that for  $k_f$  due to the large energy difference of  $\sim 6$  eV between the  $\text{O} + \text{CO}$  and the  $\text{C} + \text{O}_2$  asymptotes, see Fig. 1. There are, however, computational investigations of the oxidation of  $\text{CO}$  to form  $\text{CO}_2$  following the  $\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+) \rightarrow \text{CO}_2(^1\Sigma_g^+)$  route, usually involving a third particle  $\text{M}$ .<sup>16</sup> The rates for formation of  $\text{CO}_2$  along the  $^3\text{A}'$  and  $^3\text{A}''$  pathways starting from  $\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+)$  ranged from  $10^{-13}$  to  $10^{-12}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , depending on temperature, compared with  $\sim 10^{-14}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from earlier work.<sup>17</sup> These were non-Born–Oppenheimer dynamics simulations of the  $\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+) \rightarrow \text{CO}_2(^1\Sigma_g^+)$  reaction involving the  $^1\text{A}'$ ,  $^3\text{A}'$ , and  $^3\text{A}''$  potential energy surfaces (PESs).<sup>16</sup> The spin-forbidden fraction in this study was, however, found to be small ( $\sim 1\%$ ). Experimentally, the forward reaction has not been probed so far, to the best of our knowledge. Direct experiments involving  $[\text{O}(^3\text{P}), \text{O}(^1\text{D})]$  and  $\text{CO}(^1\Sigma^+)$  concern the vibrational deactivation of  $\text{CO}$  upon collision with atomic oxygen.<sup>2,18–21</sup> Finally, the rate for the  $\text{O}(^1\text{D})$  to  $\text{O}(^3\text{P})$  spin relaxation by  $\text{CO}(^1\Sigma^+)$  at temperatures between 113 and 333 K was determined.<sup>22</sup> The rates were found to vary monotonically from about  $7.6 \times 10^{-11}$  to  $5.2 \times 10^{-11}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range. Earlier modeling based on collisions with  $\text{CO}$  and other small molecules obtained a rate of  $8 \times 10^{-11}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>23</sup>

Computationally, the ground and excited state PESs for  $\text{CO}_2$  have been studied in some detail.<sup>13,24–29</sup> Early configuration

interaction calculations established<sup>24</sup> that there must be four states (two singlet and two triplet) of  $\text{CO}_2$  below the  $\text{CO}(^1\Sigma^+) + \text{O}(^3\text{P})$  asymptote which is also what is found in the present work (Fig. 1).  $\text{CO}_2$  does not show strong absorptions below 11 eV<sup>24</sup> which makes direct comparison difficult also, because often vertical and not adiabatic transition energies were measured. A low-lying adiabatic electronic transition to a triplet state was reported at  $39\,412 \text{ cm}^{-1}$  (4.89 eV) above the ground state,<sup>30</sup> in qualitative agreement with the position of the  $^3\text{A}'$  state, 4.62 eV above the ground state, see Fig. 1.

An early classical MD study<sup>31</sup> of the forward reaction using an analytical potential energy surface found a rate of  $k_f = 1.92 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . In dynamics studies<sup>16,18,28,32,33</sup> the reference energies from electronic structure calculations were either represented as parametrized fits,<sup>18,32,33</sup> cubic splines,<sup>28</sup> or interpolated moving least squares.<sup>16</sup> Reference calculations were carried out at the CASSCF-MP2/631G+(d),<sup>18</sup> and MRCI+Q/aug-cc-pVQZ levels of theory.<sup>16,28,33</sup> The dynamics simulations either concerned the O-induced collisional dissociation of  $\text{CO}$ ,<sup>33</sup>  $\text{CO}$  vibrational relaxation,<sup>18</sup> the O-exchange dynamics in reactive  $\text{O} + \text{CO}$  collisions,<sup>16</sup> or the final state distributions from the  $\text{O} + \text{CO}$  reactive scattering<sup>32</sup> but not the entire  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}_2 \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})/\text{O}(^3\text{P})$  reaction involving several electronic states.

A schematic of the states derived from the present calculations and considered in the present work is provided in Fig. 1. The left hand side is the  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$  (entrance) channel which connects to all bound  $\text{CO}_2$  states in the middle. This asymptote is 11.22 eV above the global minimum which is the linear  $\text{CO}_2(^1\text{A}')$  structure. The right hand side of Fig. 1 shows the two product channels considered: the lower  $\text{CO}(^1\Sigma^+) + \text{O}(^3\text{P})$  state, 5.30 eV above the minimum energy of the  $\text{CO}_2(^1\text{A}')$  ground state, and the  $\text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})$  asymptote another 1.97 eV higher in energy. The final state involving  $\text{O}(^3\text{P})$  connects with the triplet states ( $^3\text{A}'$  and  $^3\text{A}''$ ) of  $\text{CO}_2$  whereas that leading to  $\text{O}(^1\text{D})$  correlates with the  $^1\text{A}'$ ,  $^1\text{A}''$ , and  $(2)^1\text{A}'$  states, see Fig. 1.

Except for the shock tube experiments<sup>35</sup> on  $\text{C} + \text{O}_2 \rightarrow \text{O} + \text{CO}$  (1500–4200 K) and the computations<sup>16</sup> for  $\text{CO}_2$  formation from  $\text{O} + \text{CO}$  (between 1000 K and 5000 K) there is little information on the high-temperature dynamics of either, the  $\text{C} + \text{O}_2$  or the  $\text{O} + \text{CO}$  reactive processes. The present work extends this by performing QCT simulations on the 5 lowest states of  $\text{CO}_2$ , represented as a reproducing kernel Hilbert space (RKHS),<sup>36,37</sup> and focusing on the forward and reverse reactions and vibrational relaxation. First, the methods are presented and the potential energy surfaces for all 5 states are discussed. Then the thermal rates are determined along the singlet pathway. Next, vibrational relaxation for the  $\text{O} + \text{CO}$  collision is considered for  $\text{CO}(\nu = 1)$  and  $\text{CO}(\nu = 2)$  and the distributions for relaxing/nonrelaxing reactive/nonreactive trajectories are mapped onto the PES. Finally, conclusions are drawn.

## Computational methods

This section presents the generation and representation of the potential energy surfaces and the methodologies for the QCT simulations and their analysis.



## Electronic structure calculations

All PESs are computed at the multi reference CI singles and doubles (MRCISD) level of theory<sup>38,39</sup> including the Davidson quadruples correction<sup>40</sup> (MRCISD+Q) together with the aug-cc-pVTZ basis set<sup>41</sup> using the MOLPRO 2019.1 software.<sup>42</sup> In order to consistently describe all relevant states and avoid numerical instabilities due to closely-lying states of the same symmetry, state-averaged CASSCF<sup>43–46</sup> calculations including the two lowest states of each symmetry (two spin symmetries and two spatial symmetries) were carried out. Hence, in total eight states are included in the CASSCF reference wave function. MRCISD+Q calculations for both asymptotic channels followed for the 5 lowest CO<sub>2</sub> states, namely <sup>1</sup>A', <sup>3</sup>A', <sup>3</sup>A'', <sup>1</sup>A'', and (2)<sup>1</sup>A', see Fig. 1.

The energies were computed on a grid defined by Jacobi coordinates ( $r, R, \theta$ ) where  $r$  is the separation of the diatomic,  $R$  is the distance between the atom and the center of mass of the diatomic and  $\theta$  is the angle between the two unit vectors  $\vec{r}$  and  $\vec{R}$ . For channel I (C(<sup>3</sup>P) + O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>−</sup>)) the  $R$ -grid included 28 points between 1.4 and 11 $a_0$  and the distance  $r$  was covered by 20 points between 1.55 and 4.10 $a_0$  whereas for channel II (O(<sup>3</sup>P/<sup>1</sup>D) + CO(<sup>1</sup>Σ<sup>+</sup>)) the  $R$ -grid included 26 points between 1.8 and 11 $a_0$ , and the distance  $r$  was covered by 20 points between 1.55 and 4.00 $a_0$ . The angular grid for both channels contained 13 angles from a Gauss–Legendre quadrature (169.796°, 156.577°, 143.281°, 129.967°, 116.647°, 103.324°, 90.100°, 76.676°, 63.353°, 50.033°, 36.719°, 23.423°, 10.204°).

The reference points are then represented using reproducing kernel Hilbert space (RKHS) techniques.<sup>36,37,47</sup> The quality of the representation is further checked using energies from additional, off-grid geometries. The global, reactive 3D PES  $V(r_1, r_2, r_3)$  for an electronic state is constructed by summing the weighted individual PESs for each channel

$$V(r_1, r_2, r_3) = \sum_{j=1}^3 w_j(r_j) V_j(R, r_j, \theta), \quad (1)$$

using an exponential switching function with weights

$$w_i(r) = \frac{e^{-(r_i/\sigma_i)^2}}{\sum_{j=1}^3 e^{-(r_j/\sigma_j)^2}}. \quad (2)$$

Here,  $\sigma_i$  are switching function parameters for channels I and II. These parameters were optimized by a least squares fit and yielded values of (0.90, 1.00, 1.00) $a_0$ , (1.10, 1.05, 1.05) $a_0$ , (0.9, 1.00, 1.00) $a_0$ , (0.85, 1.25, 1.25) $a_0$  and (1.05, 1.00, 1.00) $a_0$  for the <sup>1</sup>A', (2)<sup>1</sup>A', <sup>1</sup>A'', <sup>3</sup>A', and <sup>3</sup>A'' PESs, respectively.

The global and local minima and transition states between the minima and/or entrance channels supported by the PESs were determined using BFGS minimization and the nudged elastic band method<sup>48</sup> as implemented in the atomic simulation environment (ASE).<sup>49</sup>

## Quasi-classical trajectory simulations

The QCT simulations used in the present work have been extensively described in the literature.<sup>50–53</sup> Here, Hamilton's

equations of motion are solved using a fourth-order Runge–Kutta method. The time step was  $\Delta t = 0.05$  fs which guarantees conservation of the total energy and angular momentum and the initial separation of the reactants was 19 $a_0$ . Fig. S2 (ESI†) reports reference energies from electronic structure calculations (open symbols) with the resulting RKHS PES for a given angular cut out to a distance of  $r = 40a_0$ . The maximum impact parameter  $b_{\max}$  was 15.0 $a_0$  (at low  $T$  and for low collision energy) and was reduced to 8.0 $a_0$  for rate calculations at the highest temperatures. Initial conditions for the trajectories are sampled using standard Monte Carlo methods.<sup>50</sup> The reactant and product ro-vibrational states are determined following semi-classical quantization with quantum bound state calculations for the two diatomics. Since the ro-vibrational states of the product diatom are continuous numbers, the states need to be assigned to integer values for which a Gaussian binning (GB) scheme was used. For this, Gaussian weights centered around the integer values with a full width at half maximum of 0.1 were used.<sup>52,54,55</sup> It is noted that using histogram binning (HB) was found to give comparable results for a similar system.<sup>53</sup>

The thermal rate for an electronic state ( $i$ ) at a given temperature ( $T$ ) is then obtained from

$$k_i(T) = g_i(T) \sqrt{\frac{8k_B T}{\pi \mu}} \pi b_{\max}^2 \frac{N_r}{N_{\text{tot}}}, \quad (3)$$

where  $g_i(T)$  is the electronic degeneracy factor of state ' $i$ ',  $\mu$  is the reduced mass of the collision system,  $k_B$  is the Boltzmann constant, and, depending on the specific process considered,  $N_r$  is the number of reactive or vibrationally relaxed trajectories. In the rate coefficient calculations, the initial ro-vibrational states and relative translational energy (collision energy  $E_c$ ) of the reactants for the trajectories are sampled from Boltzmann and Maxwell–Boltzmann distributions at given  $T$ , respectively. The sampling methodology is discussed in detail in ref. 53.

For the forward C(<sup>3</sup>P) + O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>−</sup>) → CO(<sup>1</sup>Σ<sup>+</sup>) + O(<sup>1</sup>D) and reverse reactions CO(<sup>1</sup>Σ<sup>+</sup>) + O(<sup>1</sup>D) → C(<sup>3</sup>P) + O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>−</sup>) with rates  $k_f(T)$  and  $k_r(T)$ , respectively, the degeneracy factor is

$$g_{(1A', (2)1A', 1A'')} (T) = \frac{1}{\left(1 + 3 \times e^{\frac{-23.6}{T}} + 5 \times e^{\frac{-62.4}{T}}\right)} \quad (4)$$

where the terms are the degeneracies of the carbon J-states for which the energy differences between the ground and the excited states are 23.6 K and 62.4 K, respectively.<sup>56</sup> For the reactions leading to O(<sup>3</sup>P) and going through triplet CO<sub>2</sub> the degeneracies are  $g_{(3A', 3A'')} = \frac{1}{3}$ . From  $k_f(T)$  and  $k_r(T)$  the equilibrium constant

$$K_{\text{eq}}(T) = \frac{k_f(T)}{k_r(T)} \quad (5)$$

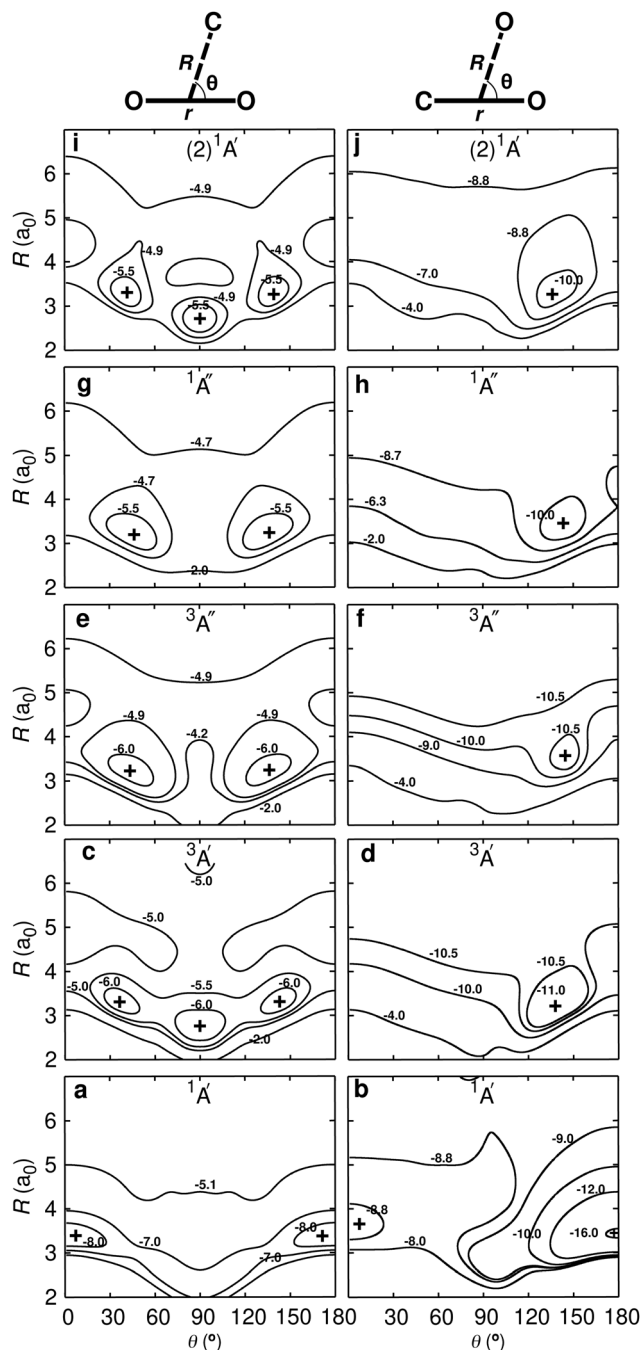
is determined.



## Results

### The potential energy surfaces

Two-dimensional contour plots of the PESs are shown in Fig. 2 and the positions and relative energies of the critical points are summarized in Table 1. The left hand column in Fig. 2 reports



**Fig. 2** Two-dimensional cuts through the 3-d PES for the OO + C (left) and the CO + O (right) channels. Energy contours (in eV) for the  $1A'$  (panels a and b),  $3A''$  (panels c and d),  $3A'$  (panels e and f),  $1A''$  (panels g and h), and  $(2)1A'$  (panels i and j) states. The OO and CO diatomic distance are fixed at  $r = 2.14$  and  $r = 2.29a_0$  for the CO + O and OO + C channels, respectively. The zero of energy is the dissociation into atomic fragments ( $C(^3P) + O(^3P) + O(^3P)$ ). The symbol ("+") indicates local and global minima on each PES.

the PESs for the C + O<sub>2</sub> asymptote whereas the right hand column that for the CO + O channel, including the linear ground state structure for CO<sub>2</sub> (Fig. 2b). All PESs for the C + O<sub>2</sub> asymptote are manifestly symmetric with respect to  $\theta = 90^\circ$  with moderate anisotropies for the  $1A'$  and  $3A'$  states and increased anisotropies for all other PESs. Conversely, all PESs for the O + CO channel are single-minima PESs with their minima around  $140^\circ$ , except for the  $1A'$  state which has a minima for the OCO ( $180^\circ$ ) and OOC ( $0^\circ$ ) structures, see also Fig. S3 (ESI<sup>†</sup>). The energy of the OOC state is  $170.0 \text{ kcal mol}^{-1}$  (7.37 eV) above the OCO minimum and the barrier height for transition between the OOC and OCO minima is  $8.5 \text{ kcal mol}^{-1}$  (0.369 eV). In addition, the existence of the local OOC minimum was confirmed at the MRCISD+Q and CCSD(T) levels of theory and was suggested earlier from experiments<sup>11,12</sup> and calculations.<sup>13</sup>

The quality of the RKHS representations is reported in Fig. S4 (ESI<sup>†</sup>). All root mean squared errors for both, on-grid and off-grid points are below  $1 \text{ kcal mol}^{-1}$  (0.043 eV), except for the  $1A''$  PES for which it is  $1.04 \text{ kcal mol}^{-1}$  (0.045 eV), all evaluated on the mixed PESs, see eqn (1) and (2). For the individual channels the performance of the RKHS is even better. One dimensional cuts for an OCO angle of  $120^\circ$  directly comparing the reference points and the RKHS are shown in Fig. S5 (ESI<sup>†</sup>) for the lowest five states. Importantly, for off-grid points which were not used to construct the PESs but to independently validate the RKHS representations, the RMSEs are all below  $1 \text{ kcal mol}^{-1}$  (0.043 eV), too.

For a better understanding of the shapes of the PESs, the SA-CASSCF/aug-cc-pVTZ wave functions were analyzed in more detail for the different states at a bent geometry ( $\theta = 117.65^\circ$ ), see Fig. 3, for  $r_{CO} = 2.14a_0$  and varying  $R$ . Fig. 3A shows the valence molecular orbitals that are relevant for the description of the eight states in the SA-CASSCF calculations along the CO<sub>2</sub> → CO + O dissociation for this bent geometry. Fig. 3B depicts the dominant configuration state functions along this dissociation path. All states except for the energetically high lying  $(2)3A'$  state resolve with one dominant CASSCF configuration state function for the eight computed states of SA-CASSCF and keep their characteristic configuration along the entire dissociation path. Hence, no avoided crossing of two states with the same symmetry is observed. Fig. 3C shows the relative energetics (taking the  $C(^3P) + O(^3P) + O(^3P)$  ground state computed with the same level of theory as the reference).

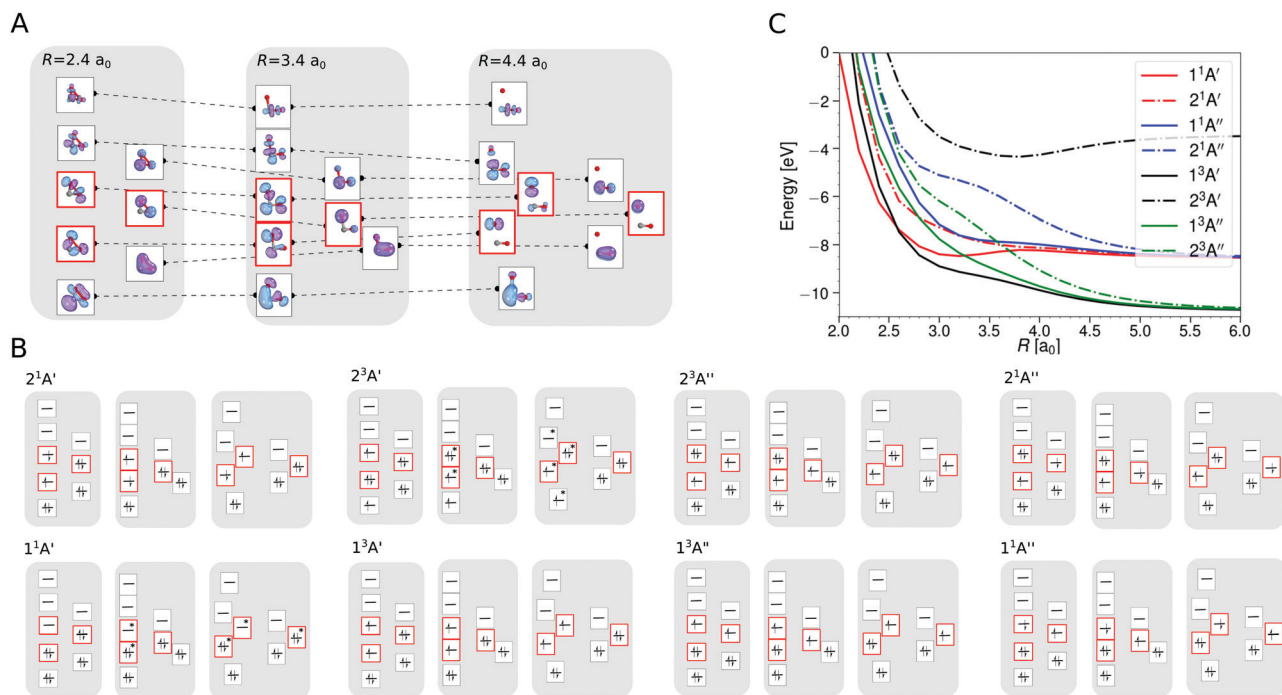
Upon bending, the doubly degenerate  $\pi_3$  non-bonding [doubly occupied in  $1A'$ ], as well as the  $\pi_3$  antibonding [unoccupied in  $1A'$ ] orbitals for collinear CO<sub>2</sub> undergo a splitting due to the lifted degeneracy. This results in a Jahn–Teller splitting of the states  $1A''$ ,  $3A''$ ,  $3A'$ , and  $(2)1A'$  of CO<sub>2</sub> with their energy minimum at a bent geometry, see right hand column in Fig. 2. The splitting of the degenerate HOMO and LUMO  $\pi_3$  orbitals upon bending leads to three frontier orbitals, similar in energy, and with overall occupation of four electrons in all five energetically low-lying states (red frames in Fig. 3A). One of these three frontier orbitals has  $\sigma^*$  character along the O–O bond (see Fig. 3A) and is somewhat higher in energy. States that involve double occupation of this orbital lie higher in energy. Along the same line, states that





**Table 1** Minima (MIN*i*) and transition states (TS*i*) on the CO<sub>2</sub> PESs towards the CO(<sup>1</sup>Σ<sup>+</sup>) + O(<sup>3</sup>P) asymptote using the Nudged Elastic Band (NEB) method.<sup>48</sup> The PESs are in ascending energetic order, see Fig. 2. Distances are in a<sub>0</sub> and Energy in eV. Energies relative to the CO(<sup>1</sup>Σ<sup>+</sup>) + O(<sup>3</sup>P) dissociation limit. Present values are compared with previous work: for triplet states top row ref. 16, bottom row ref. 18. For the global minimum in the <sup>1</sup>A' state: top row experiment,<sup>57</sup> bottom row ref. 16 and for the remaining minima and transition states ref. 58. Where necessary, literature values were converted to a<sub>0</sub> and eV

PES	Present work				Literature <sup>16,18,57–59</sup>			
	<i>r</i> <sub>1</sub> (CO <sub>A</sub> )	<i>r</i> <sub>2</sub> (CO <sub>B</sub> )	∠(OCO)	<i>E</i> (eV)	<i>r</i> <sub>1</sub>	<i>r</i> <sub>2</sub>	∠(OCO)	<i>E</i> (eV)
(2) <sup>1</sup> A' MIN	2.368	2.368	119.0	0.23	—	—	—	—
<sup>1</sup> A'' MIN	2.374	2.374	130.5	−0.13	—	—	—	—
<sup>3</sup> A'' MIN	2.374	2.374	130.6	−0.14	2.364	2.364	127.2	−0.23
<sup>3</sup> A'' TS	2.165	3.431	135.8	0.47	2.399	2.399	127.0	−0.22
					2.147	3.515	126.2	0.35
					2.192	3.496	122.0	0.30
<sup>3</sup> A' MIN	2.356	2.356	126.3	−0.69	2.381	2.381	118.0	−0.94
					2.349	2.349	118.0	−0.92
					2.143	3.628	120.8	0.28
<sup>3</sup> A' TS	2.163	3.544	116.3	0.39	2.192	3.779	112.0	0.20
					2.196	2.196	180.0	−5.45
					2.194	2.194	180.0	−5.64
<sup>1</sup> A' (Global-M)	2.206	2.206	180.0	−5.30	2.522	2.522	72.9	0.61
<sup>1</sup> A' (MIN1)	2.527	2.527	70.6	0.74	2.220	4.716	0.0	1.72
<sup>1</sup> A' (MIN2)	2.192	4.798	0.0	1.88	2.600	2.309	91.8	1.04
<sup>1</sup> A' (TS1)	2.502	2.430	88.4	1.05	2.203	4.537	41.0	2.22
<sup>1</sup> A' (TS2)	2.164	4.279	68.9	2.15				



**Fig. 3** Analysis of the all-valence active space SA-CASSCF/aug-cc-pVTZ wave functions for a bent geometry with  $\theta = 117.65^\circ$ ,  $r_{\text{CO}} = 2.14a_0$  and for  $R = 2.4, 3.4, 4.4a_0$  (CO<sub>2</sub> → CO + O dissociation path). (A) Valence molecular orbitals (natural orbitals) energetically close to the three frontier orbitals (red frames) whose occupation defines the five lowest lying electronic states considered for the dynamics on the CO<sub>2</sub> PES. The three depicted geometries are oriented with the symmetry plane parallel to the paper plane. Orbitals symmetric and antisymmetric with respect to the plane in the left and right columns of each diagram, respectively. (B) Dominant configuration state functions of the eight states included in the SA-CASSCF calculation depicted as MO diagrams of the orbitals presented in panel A. If other configurations contributed with a weight > 0.05, the orbitals involved in the entanglement are marked by an asterisk (i.e. these orbitals have an occupation number that deviates significantly from the depicted integer value). (C) Energy curves of the eight states for the CO<sub>2</sub> → CO + O dissociation at this bent geometry. The ground state C + O + O energy computed at the same level of theory is the reference energy.



involve single occupation of one of the strongly bonding orbitals below the frontier orbitals also lie energetically higher.

The  $^3A'$  and  $^3A''$  states are lower in energy than the  $^1A'$  state for certain bent geometries (see Fig. 2 and 3C), as the triplet states gain from increased Pauli exchange, as well as reduced Coulomb repulsion due to the single occupations of orbitals. The corresponding open shell singlet states  $[(2)^1A'$  and  $^1A'']$  lie slightly higher in energy than their triplet counterparts due to reduced Pauli exchange.

All  $CO_2$  singlet states connect to  $CO(^1\Sigma^+) + O(^1D)$  upon dissociation whereas the  $^3A'$ ,  $^3A''$ , and  $(2)^3A''$  states connect to the  $CO(^1\Sigma^+) + O(^3P)$  state. On the other hand, the  $(2)^3A'$  connects to the energetically high-lying excited  $CO(^3\Pi) + O(^3P)$  state. The low-lying triplet  $CO_2$  states have no or rather low barriers towards their dissociation across the entire PES (see Fig. 2 and 3C). Specifically, the  $(2)^3A''$  state connects to the ground state of  $CO + O$  and crosses the singlet states upon dissociation. The crossing should nevertheless only lead to negligible non-adiabatic transition rates, as they are spin-forbidden. Since this state involves double occupation of an orbital with  $\sigma^*$  character of the O–O bond, it correlates with high lying excited states in the  $C + O_2$  channel and is energetically well separated from the  $^3A''$  state whenever there are short O–O distances. It is therefore sufficient to take its occupation only into account *via* the degeneracy of  $O(^3P)$  in the quasi-classical treatment of the  $CO + O$  dissociation channel.

### Forward and reverse rates and the equilibrium constants

The forward reaction  $C(^3P) + O_2(^3\Sigma_g^-)$  (Fig. 1) generates ground and excited state oxygen ( $^3P$  and  $^1D$ ). The pathway to yield  $^3P$  involves the  $^3A'$  and  $^3A''$   $CO_2$  PESs whereas that to form  $^1D$  goes through the  $^1A'$ ,  $(2)^1A'$ , and  $^1A''$  states. For each of the reactions on each PES a minimum of  $5 \times 10^5$  trajectories was run at each temperature.

Fig. 4 shows the total thermal rates for formation of  $O(^1D)$  and  $O(^3P)$ . The rates for formation of  $O(^1D)$  start at  $1.72 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 15 K, drop to  $5.19 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $T \sim 600 \text{ K}$  and then monotonically increase to  $3.23 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for higher temperatures, see red line for the total rate in Fig. 4 with explicit numerical values reported in Table S1 (ESI<sup>†</sup>) which also reports the number of reactive trajectories that contribute to the rate. Experimentally, the total rate for this process was determined over the temperature range from 1500 K to 4000 K.<sup>35</sup> Evaluating the reported expression

$$k(T) = 1.2 \times 10^{14} e^{\frac{-2010 \text{ K}}{T}} (\pm 50\%) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 1500 \text{ K and } 4000 \text{ K yields rates of } k(1500) = 5.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k(4000) = 1.21 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \text{ This compares with } k(1500) = 5.96 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } k(4000) = 1.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ respectively, from the present simulations. A high temperature measurement at } 8000 \text{ K, associated with a substantial uncertainty, yields } k \sim 5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.^{60}$$

The inset of Fig. 4 reports the low-temperature results. Starting at 15 K the rate first decreases, goes through a minimum

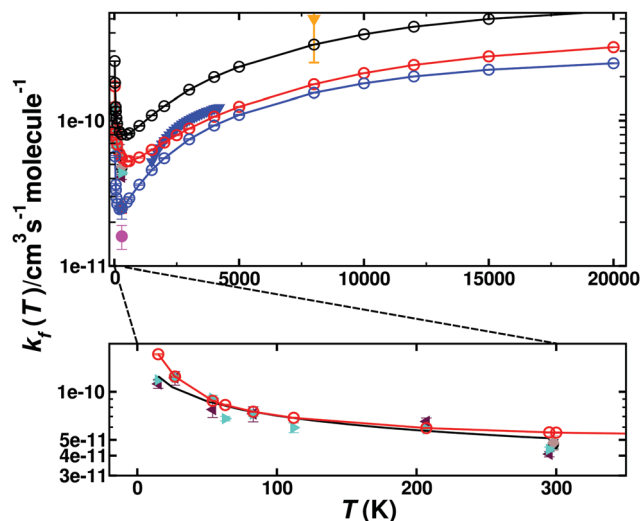


Fig. 4 Thermal rate for the forward reaction  $C(^3P) + O_2(^3\Sigma_g^-) \rightarrow CO(^1\Sigma^+) + O(^1D)/O(^3P)$ . The sum of the contribution of the singlet (red circles) and triplet (blue circles) states and the total rate (black circles). Comparison with forward rates from experiments: ref. 35 (solid blue triangles) ref. 8 (solid green right triangle), ref. 7 (solid magenta circle), ref. 6 (solid black circle), ref. 4 (solid blue square), ref. 5 (grey diamond), ref. 60 (solid orange triangle down) and ref. 3 (red triangle). The bottom panel shows an enlarged view for  $0 < T < 300 \text{ K}$  for the total singlet rate (solid red line) together with the experimental results and a fit using Arrhenius parameters provided in the literature<sup>5</sup> (inset, black solid line).

(at  $\sim 600 \text{ K}$ ) before it raises again for higher temperatures. Such a behaviour is indicative of a submerged barrier<sup>61</sup> which, based on the rates for individual surfaces, appears to be dominated by the  $^1A'$  and  $^3A'$  states, as seen in Fig. S6 (ESI<sup>†</sup>). Compared with experiments all computed rates are within 2% to 20% at 50 K and 30% to 40% for ref. 9 and 4% to 30% at 300 K for ref. 5 which can be considered good agreement. For the process to yield  $O(^3P)$  the individual rates from the contribution of both triplet PESs ( $^3A'$  and  $^3A''$ ) as well as the total weighted sum from the process to yield  $O(^1D)$  and  $O(^3P)$  are also reported in Fig. 4 (blue and black lines), with numerical values given in Table S2 (ESI<sup>†</sup>).

For the reverse reaction,  $CO(^1\Sigma^+) + O(^1D)/O(^3P) \rightarrow C(^3P) + O_2(^3\Sigma_g^-)$ , similar simulations were carried out. As this is an uphill process (Fig. 1), this channel only opens at higher temperature, see Fig. 5. The dynamics for  $CO(^1\Sigma^+) + O(^1D) \rightarrow C(^3P) + O_2(^3\Sigma_g^-)$  involves the  $^1A'$ ,  $(2)^1A'$ , and  $^1A''$  states (for numerical values see Table S3, ESI<sup>†</sup>), whereas that for  $CO(^1\Sigma^+) + O(^3P) \rightarrow C(^3P) + O_2(^3\Sigma_g^-)$  is related to the  $^3A'$  and  $^3A''$  states, given in Table S4 (ESI<sup>†</sup>). Compared with the forward rates, those for the reverse reaction are typically 1 to 5 orders of magnitude smaller. The reverse rates starting from  $O(^1D)$  are larger by 1 to 2 orders of magnitude at high  $T$  than those from  $O(^3P)$  which is consistent with the Boltzmann-weighted energy difference for the two asymptotes.

Table 2 summarizes the parameters from fitting the raw data to a modified Arrhenius expression  $k(T) = AT^n \exp(-\varepsilon/T)$  for the forward and reverse processes for all five PESs. The temperature range covers 5000 to 20 000 K as the  $CO(^1\Sigma^+) + O(^1D) \rightarrow C(^3P) + O_2(^3\Sigma_g^-)$  only opens above 5000 K. It is noted that all forward



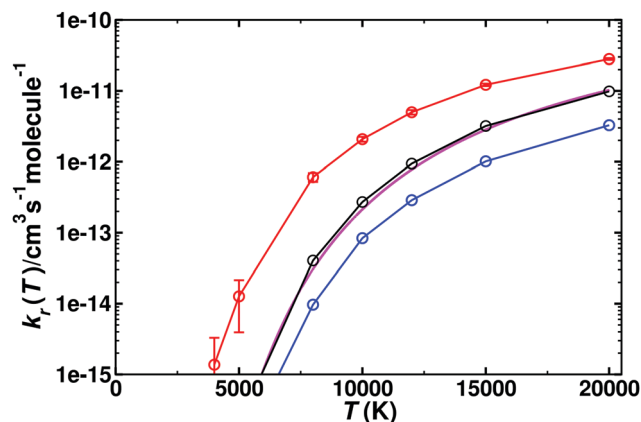


Fig. 5 Thermal rate for the reverse ( $k_r$ ) reaction  $\text{CO}(^1\Sigma^+) + \text{O}(^1\text{D}) \rightarrow \text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$ . The sum of the contributions of the singlet (red circles, with error bars from bootstrapping) and triplet (blue circles) states and their Boltzmann-weighted sum (black circles). The temperature range is from 5000–20 000 K. Comparison with recent theoretical work<sup>33</sup> (magenta solid line).

processes involve a comparatively small activation energy  $\varepsilon$  of a few hundred to a few thousand kelvin. All reverse rates have activation energies that are at least one order of magnitude larger. The number of trajectories that contribute to these rates varies from less than 1% to 55%. For the slowest process, the reverse reaction on the  $^3\text{A}'$  and  $^3\text{A}''$  PESs originating from  $\text{O}(^3\text{P})$ , at least an additional  $5 \times 10^5$  trajectories were run at each temperature between 3000 K and 20 000 K and close to  $10^6$  trajectories for  $T \leq 1000$  K.

From the forward and reverse rates the equilibrium constant  $K_{\text{eq}}(T)$  can also be determined, see Fig. 6. This equilibrium constant was determined from the total forward and reverse fluxes of the weighted sum of the singlet and triplet pathways according to the data summarized in Table 2. Error bars for the individual rates have been determined from bootstrapping and are compared with results determined from statistical mechanics. The equilibrium constant is only reported for temperatures 5000 K

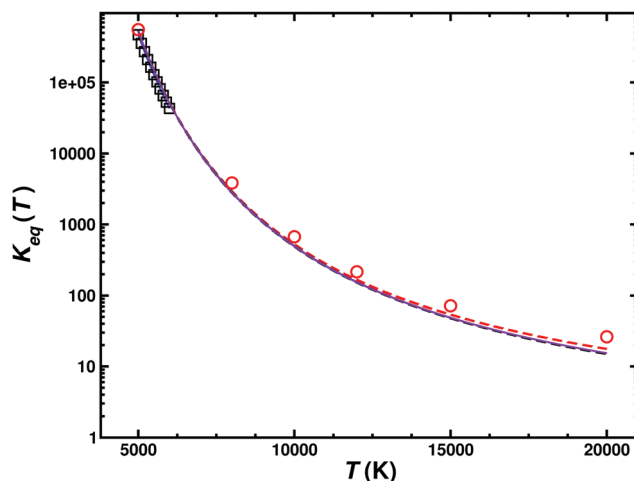


Fig. 6 Equilibrium constant for the  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})$  ( $k_1$ ) and  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \leftrightarrow \text{CO}(^1\Sigma^+) + \text{O}(^3\text{P})$  ( $k_2$ ) reactions. The results from the JANNAF tables<sup>62</sup> (black open squares), those derived from equilibrium statistical mechanics ( $k_1$  (red open circles and red dashed line),  $k_2$  (black dashed line) and their Boltzmann-weighted total  $wk_1 + (1-w)k_2$  (purple solid line)) with those from the QCT simulations are compared.

and higher as the reverse reaction only opens at these temperatures, see Fig. 5.

A final process considered is the atom exchange reaction  $\text{CO}_\text{A}(^1\Sigma^+) + \text{O}_\text{B}(^3\text{P}) \rightarrow \text{CO}_\text{B}(^1\Sigma^+) + \text{O}_\text{A}(^3\text{P})$ . For this process, on the  $^3\text{A}'$  state, rates ranging from  $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to  $6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  between 500 K and 20 000 K were found, see Table S5 and Fig. S7 (ESI<sup>†</sup>). The rate increases monotonically from values  $\sim 10^{-16}$ , consistent with those measured experimentally,<sup>63</sup> as a function of  $T$  and is smaller than the measurement at 1820 K.<sup>64</sup> One possible explanation is that this experimental value was an indirect measurement that required the decomposition rate for  $\text{N}_2\text{O}$  and is presented without derived error bars. The barrier for the atom exchange reaction inferred from the low-temperature experiments is

**Table 2** Modified Arrhenius three-parameter model for the forward  $\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \rightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})/\text{O}(^3\text{P})$  and reverse  $\text{O}(^1\text{D})/\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+) \rightarrow \text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$  reaction.  $A$  in units of  $\text{cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$  and  $\varepsilon$  in kelvin. The temperature range for the modified Arrhenius fit is 5000 to 20 000 K

Forward	$A$	$n$	$\varepsilon$
$\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \rightarrow \text{CO}(^1\Sigma^+) + \text{O}(^1\text{D})$	$4.12 \times 10^{-12}$	0.45	2209
$^1\text{A}'$	$2.42 \times 10^{-12}$	0.40	116
$(2)^1\text{A}'$	$1.21 \times 10^{-12}$	0.47	4506
$^1\text{A}''$	$1.06 \times 10^{-12}$	0.27	6639
$\text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-) \rightarrow \text{CO}(^1\Sigma^+) + \text{O}(^3\text{P})$	$3.50 \times 10^{-11}$	0.22	3513
$^3\text{A}'$	$1.60 \times 10^{-11}$	0.22	1891
$^3\text{A}''$	$5.49 \times 10^{-11}$	0.11	6789
Total	$1.56 \times 10^{-11}$	0.30	3018
Reverse			
$\text{O}(^1\text{D}) + \text{CO}(^1\Sigma^+) \rightarrow \text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$	$1.15 \times 10^{-10}$	0.11	49 965
$^1\text{A}'$	$1.25 \times 10^{-12}$	0.42	42 273
$(2)^1\text{A}'$	$4.60 \times 10^{-12}$	0.32	50 111
$^1\text{A}''$	$5.28 \times 10^{-13}$	0.53	46 836
$\text{O}(^3\text{P}) + \text{CO}(^1\Sigma^+) \rightarrow \text{C}(^3\text{P}) + \text{O}_2(^3\Sigma_g^-)$	$1.52 \times 10^{-12}$	0.50	68 903
$^3\text{A}'$	$8.92 \times 10^{-14}$	0.70	64 167
$^3\text{A}''$	$7.80 \times 10^{-09}$	-0.37	83 013
Total	$1.55 \times 10^{-10}$	0.09	71 735

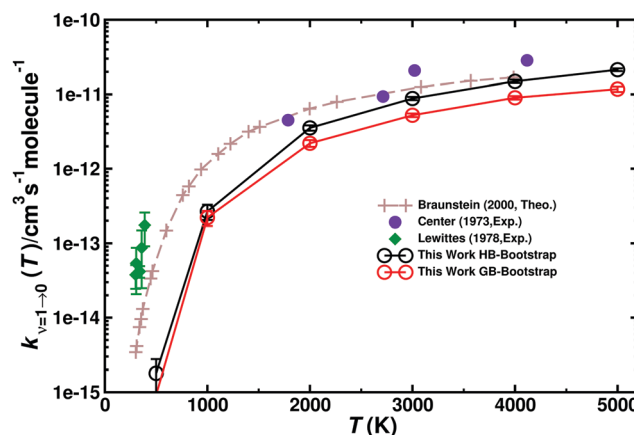


Fig. 7 Total vibrational relaxation rate for  $\text{O} + \text{CO}(\nu = 1) \rightarrow \text{O} + \text{CO}(\nu = 0)$ . Total contribution ( $^3\text{A}' + ^3\text{A}''$ ) (closed black circles) ( $g(e) = 1/3$ ). Literature values are the symbols as indicated.<sup>2,18,20</sup>  $5 \times 10^5$  trajectories were run at every temperature. Open black circles from HB and open red circles from GB with error bars from bootstrapping.





**Table 3** Vibrational relaxation rates (in units of  $10^{13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  $k_{\nu \rightarrow \nu'}$  for the collision of  $\text{O}(^3\text{P})$  with  $\text{CO}(^1\Sigma_g)$ :  $\text{O} + \text{CO}(\nu = 1) \rightarrow \text{O} + \text{CO}(\nu' = 0)$  for the  $^3\text{A}'$ ,  $^3\text{A}''$ , and  $(2)^3\text{A}''$  states and the total contribution using GB

	500 K	1000 K	2000 K	3000 K	4000 K	5000 K
$^3\text{A}'$	0.00	1.29	13.07	29.26	45.11	58.81
$^3\text{A}''$	0.00	0.87	8.97	22.70	43.87	57.21
$(2)^3\text{A}''$	0.00	0.00	0.00	0.10	0.45	1.85
Total	0.00	2.16	22.05	52.06	89.42	117.87

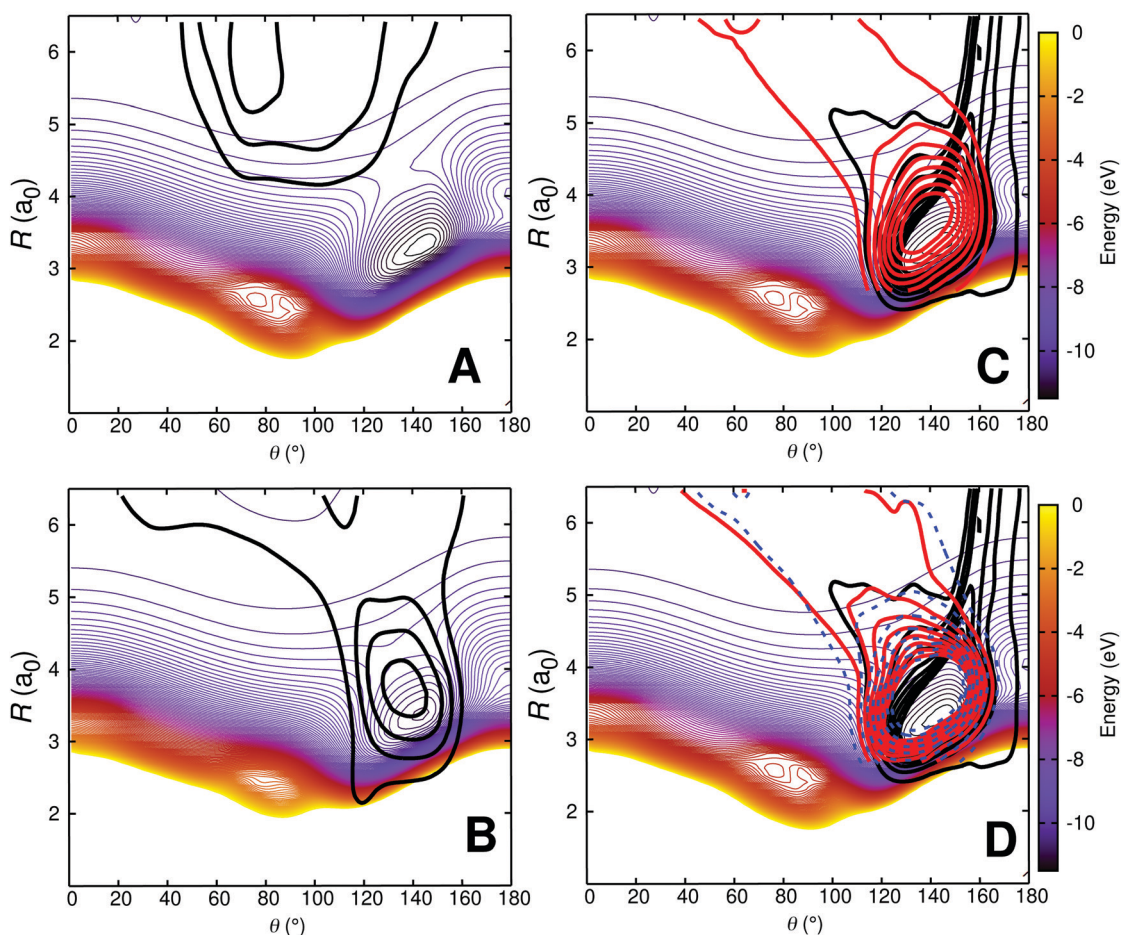
6.9 kcal mol $^{-1}$  (0.299 eV), which is also what is found from the present work (Fig. S8 and S9, ESI $^\dagger$ ).

A summary of all forward and reverse rates is provided in Fig. S6, and Tables S1–S5 (ESI $^\dagger$ ) report all numerical values for the temperature dependent rates.

### Vibrational relaxation

Vibrational relaxation (VR) of CO in its  $\nu = 1$  and  $\nu = 2$  states was investigated for both, the singlet and triplet manifolds separately. VR was investigated by running  $5 \times 10^5$  trajectories at each

temperature, ranging from 300 K to 5000 K, see Table S6 (ESI $^\dagger$ ). The final vibrational state was determined using Gaussian binning (GB) which has been shown to yield similar results as histogram binning.<sup>54,55,63</sup> Fig. 7 compares the individual and total VR rates with those measured experimentally and Table 3 reports the rates. Direct comparison with rates from Histogram binning shows that the two analyses yield a comparable  $T$ -dependence with rates from HB somewhat larger than those from GB. The computed rates are consistently lower than those from experiments at lower temperatures. For  $T > 2000$  K the rates are in good agreement with experiments, though. In order to verify that the underestimation is not due to neglect of higher electronically excited states, the  $(2)^3\text{A}''$  PES was also determined. This PES (not shown) is mainly repulsive. Therefore, the VR rates for this state only contribute  $\sim 10\%$  of the rates for the  $^3\text{A}'$  and  $^3\text{A}''$  states at the highest temperatures. Hence, the differences between experiment and simulations at lower temperatures are not due to neglect of contributions from higher-lying electronic states (Table 3).



**Fig. 8** Density map for  $\text{O} + \text{CO}(\nu = 1)$  collisions at 1000 K on the relaxed  $^3\text{A}'$  PES. Panel A:  $\text{O} + \text{CO}(\nu = 1) \rightarrow \text{O} + \text{CO}(\nu' = 1)$ ; Panel B:  $\text{O} + \text{CO}(\nu = 1) \rightarrow \text{O} + \text{CO}(\nu' = 0)$ ; Panel C:  $\text{O}_\text{A} + \text{CO}_\text{B}(\nu = 1) \rightarrow \text{O}_\text{B} + \text{CO}_\text{A}(\nu' = 1)$  and Panel D:  $\text{O}_\text{A} + \text{CO}_\text{B}(\nu = 1) \rightarrow \text{O}_\text{B} + \text{CO}_\text{A}(\nu' = 0)$ . For the reactive trajectories (panels C and D), two coordinate systems are used: one for the reactant (black density) in which the  $\text{CO}_\text{B}$  diatom is the distance  $r$  and the separation of atom  $\text{O}_\text{A}$  from the center of mass is the distance  $R$ ; the second coordinate system is for the product state (red density) for which the  $\text{CO}_\text{A}$  diatom is the distance  $r'$  and the separation of atom  $\text{O}_\text{B}$  from the center of mass is the distance  $R'$ . The dashed blue isocontours in panel D are for  $\text{O}_\text{A} + \text{CO}_\text{B}(\nu = 1) \rightarrow \text{O}_\text{B} + \text{CO}_\text{A}(\nu' = 2)$ . The density map for the trajectories is superimposed on a relaxed 2D RKHS PES where  $2.00 < r < 2.30a_0$  (turning points). For all density maps 1500 trajectories were used to generate the 2d densities which were smoothed using kernel density estimation (KDE) as implemented in the *R* software package.<sup>67</sup>





In order to better characterize to which parts of the PES the individual processes are sensitive to, density maps were determined as follows. For each initial condition a trajectory can be attributed to one of the 4 possible outcomes: (a) no vibrational relaxation, no reaction:  $O + CO(\nu = 1) \rightarrow O + CO(\nu' = 1)$  (b) vibrational relaxation without reaction:  $O + CO(\nu = 1) \rightarrow O + CO(\nu' = 0)$ , (c) no vibrational relaxation but with atom exchange:  $O_A + CO_B(\nu = 1) \rightarrow O_B + CO_A(\nu' = 1)$ , and (d) vibrational relaxation with atom exchange:  $O_A + CO_B(\nu = 1) \rightarrow O_B + CO_A(\nu' = 0)$ . Then, all trajectories for a given class were combined and a 2-dimensional histogram was generated and smoothed using kernel density estimation (KDE).<sup>66</sup> The resulting

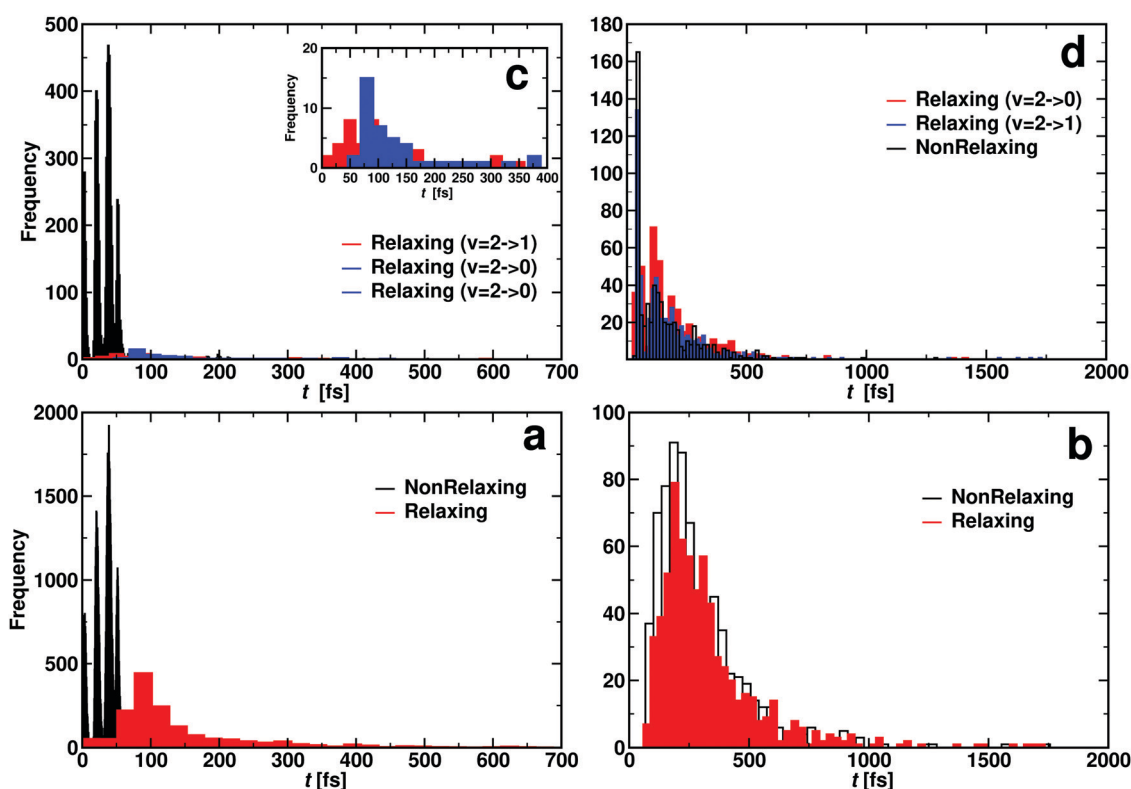
**Table 4** Average contact time ( $\tau_c$  in fs, for definition see text) and number  $N$  of trajectories for each final state for  $N_{\text{tot}} = 5 \times 10^5$  trajectories for each of the processes considered. In each case the difference  $N_{\text{tot}} - N$  are fly-by trajectories. This table reports the cases  $\nu = 2 \rightarrow x$  and  $\nu = 1 \rightarrow x$  for both reactive and non-reactive events

	Relaxing			Nonrelaxing	
	$\nu = 2 \rightarrow 1$	$\nu = 2 \rightarrow 0$	$\nu = 1 \rightarrow 0$	$\nu = 2 \rightarrow 2$	$\nu = 1 \rightarrow 1$
Reacting					
$N$	300	230	679	340	742
$\tau_c$	210	207	333	241	301
Non-reacting					
$N$	480	440	1577	65 788	117 365
$\tau_c$	126	158	156	33	36

2-dimensional distribution was then projected onto the relaxed PES for the corresponding state, see Fig. 8.

Fig. 8A shows that nonrelaxing trajectories sample regions in the long range without penetrating into the strongly interacting region around ( $R = 3.2a_0$ ,  $\theta = 150^\circ$ ). Contrary to that, nonreactive, relaxing trajectories of the type  $O + CO(\nu = 1) \rightarrow O + CO(\nu' = 0)$  access the strongly interacting region and sample it before leaving this region again, see Fig. 8B. For the reactive trajectories ( $O_A + CO_B \rightarrow O_B + CO_A$ ), see Fig. 8C and D, all trajectories enter the strongly interacting region along  $\theta \sim 160^\circ$  (black density).

After the reaction, the product ( $CO_A$ ) can either remain vibrationally excited (Fig. 8C; no relaxation), or its vibrational state can change ( $CO_A(\nu' = 0)$  or  $CO_A(\nu' = 2)$ ). The highest vibrational state in the products after reaction in these trajectories (run at 1000 K) is  $\nu' = 3$ . The probability distributions of the products from reactive collisions in Fig. 8C and D are in red (for  $\nu' = 0$ , relaxation) and in blue (for  $\nu' = 2$ , further excitation). The shape of the red and blue probability distributions in Fig. 8C and D can already be anticipated from the relaxed PES for the  $CO + O$  channel, see Fig. S10 (ESI<sup>†</sup>). Starting from around the minimum on the PES at ( $R = 3.2a_0$ ,  $\theta = 140^\circ$ ) these densities follow the path indicated by the green isocontour at  $-10.5$  eV in Fig. S10 (ESI<sup>†</sup>) through the constriction indicated as a red cross. A different perspective that could be taken is to refer to all reactive trajectories as “vibrationally relaxing” because the quanta initially present in  $CO_B$  are destroyed upon dissociation



**Fig. 9** Contact time histogram for  $O_A + CO_B \rightarrow O_B + CO_A$  (reacting: panel a and c) and  $O_A + CO_B \rightarrow O_A + CO_B$  (non reacting: panel b and d). Bottom panels for  $CO(\nu = 1)$  and top panel for  $CO(\nu = 2)$ . Panel c inset illustrates that relaxing two quanta ( $\nu = 2 \rightarrow 0$ , blue distribution) takes longer than relaxing one quantum ( $\nu = 2 \rightarrow 1$ , red distribution). Additional analysis of the data from panel c is provided in Fig. S11 (ESI<sup>†</sup>). Rates for the atom exchange reaction are given in Table S5 (ESI<sup>†</sup>).

of CO<sub>B</sub>. However, experimentally, the final states CO<sub>B</sub>( $\nu' = 1$ ) and CO<sub>A</sub>( $\nu' = 1$ ) can not be distinguished. Hence separation into 4 separate cases is meaningful in analyzing the trajectories.

It is also of interest to consider the distribution of contact times  $\tau_c$  for each of the scenarios. This quantity was taken as the first instance along the trajectory for which the sum  $\sigma$  of all three atom distances is smaller than  $12a_0$  in the entrance channel until the point at which  $\sigma > 12a_0$  along the exit channel. This was done for CO initially in its  $\nu = 1$  and  $\nu = 2$  states, respectively. The average contact times are reported in Table 4 and their distributions are shown in Fig. 9. It should, however, be noted that the average  $\tau_c$  only incompletely characterize the underlying distribution  $P(\tau_c)$  because the distributions are either structured (Fig. 9a and c) or extend to times more than 10 times the most probable value as in Fig. 9b and d.

For reacting trajectories and non-reacting but relaxing trajectories, the contact time  $\tau_c$  decreases with increasing vibrational excitation. This differs for non-reacting, relaxing trajectories. Their average contact times appear to be determined by the final vibrational state. For relaxation to  $\nu' = 0$  the average vibrational relaxation time is  $\sim 150$  fs which shortens to  $\sim 70$  fs for relaxation to  $\nu' = 1$  with initial  $\nu = 2$ . This is in contrast to the non-relaxing non-reacting trajectories which appear to be independent of vibrational excitation. The  $\tau_c$  for these trajectories is of the order of 30 fs which is roughly the minimum time required for one collision.

When considering the lifetime distributions it is found that those involving reacting trajectories display a regular pattern of peaks, see Fig. 9a and c. The specific case for relaxation from ( $\nu = 1$ )  $\rightarrow$  ( $\nu' = 0$ ) is shown in Fig. S11 (ESI<sup>†</sup>). It is noticeable that the probability to find trajectories that react but do not relax  $P(\tau_c)$  can be zero and reaches maximal values for other values for the lifetime. Fourier transformation of this signal yields frequencies between  $1824\text{ cm}^{-1}$  and  $2529\text{ cm}^{-1}$ , see Fig. S11 (ESI<sup>†</sup>). These frequencies, which are in the range of typical CO stretch frequencies, can be understood as “gating modes” that allow the reaction to occur, similar to what was found for proton transfer in protonated ammonia dimer.<sup>68</sup>

It is also of interest to consider the geometries sampled for the  $\text{C} + \text{O}_2 \rightarrow \text{CO} + \text{O}(\text{D})$  reaction on the  $^1\text{A}'$  PES depending on the temperature from which the initial conditions were generated. This was done for  $T = 15\text{ K}$  and  $T = 10\,000\text{ K}$ . For reactive trajectories at low temperature the global minimum is extensively sampled (see Fig. S12A, ESI<sup>†</sup>) whereas at high temperature this region is not sampled at all as shown in Fig. S12B (ESI<sup>†</sup>). Hence, collisions at different temperatures are expected to sample complementary regions of the 3d PES.

## Discussion and conclusions

The present work reports thermal and vibrational relaxation rates from QCT simulations on the five lowest PESs of the [COO] system. Comparison of the computed rates with experiment is favourable for thermal rates and vibrational relaxation rates at high temperatures. For the atom exchange rate, agreement is rather more qualitative, with an overall

offset in the energetics of 300 K (0.026 eV). Additional analyses are carried out in the following to provide an understanding of remaining disagreements between experiment and simulations.

One interesting comparison can be made with state-to-state cross section measurements for the  $\text{C}(\text{P}) + \text{O}_2(\text{g}^-) \leftrightarrow \text{CO}(\text{P}) + \text{O}(\text{D})$  reaction at small collision energies.<sup>34</sup> These experiments used a pulsed nozzle through which the  $\text{O}_2$  expanded into the vacuum. The  $\text{O}_2$  internal state distribution was not measured directly but expected to be very cold.<sup>34</sup> Hence, it is likely that mostly  $\text{O}_2(\nu = 0)$  with low  $j_{\text{max}}$  was populated. Such experiments found that excitation of  $\text{CO}(\nu' = 16)$  occurs for all collision energies  $E_c$  whereas population of  $\text{CO}(\nu' = 17)$  is only possible with an excess of  $E_c > 0.04\text{ eV}$ . Using bound state energies for CO derived from experiment<sup>69</sup> and accounting for the 0.04 eV required to open the  $\text{CO}(\nu' = 17)$  channel, the energy difference between  $\text{CO}(\nu = 0)$  and  $\text{CO}(\nu' = 17)$  is 4.037 eV. Including zero point energy for CO and  $\text{O}_2$ , the difference between the  $\text{C}(\text{P}) + \text{O}_2$  and  $\text{CO} + \text{O}(\text{P})$  channels from experimental data is 4.075 eV. This differs by 0.085 eV from the value at the MRCISD level of theory which is 3.990 eV.

From semiclassical calculations on the present PESs the  $\text{CO}(\nu' = 17)$  state is at 4.140 eV. This compares with the difference in electronic energies (3.990 eV) and differences in the CO and  $\text{O}_2$  zero point energies of 3.952 eV. Hence,  $E_c = (4.140 - 3.952) = 0.188\text{ eV}$  is required to open the  $\text{CO}(\nu' = 17)$  channel. QCT simulations starting from Boltzmann-distributed ( $\nu, j$ ) initial conditions generated at  $T = 2000\text{ K}$  find that the population of the  $\text{CO}(\nu' = 16)$  decays exponentially with increasing  $E_c$  (Fig. S13, ESI<sup>†</sup> left panel) which is consistent with experiments.<sup>34</sup> Because expansion through a nozzle does not necessarily yield Boltzmann-distributed initial conditions and the experimental beam was deemed “very cold”,<sup>34</sup> the final state distributions were also separated into those originating from  $\text{O}_2(\nu = 0)$  (open circles in Fig. S13, ESI<sup>†</sup>) and those from  $\text{O}_2(\nu > 0)$  (solid line in Fig. S13, ESI<sup>†</sup>). For  $\text{CO}(\nu' = 16)$  all distributions follow the same overall behaviour.

Conversely, for  $\text{CO}(\nu' = 17)$  considering the final state distribution from initial  $\text{O}_2(\nu = 0)$  has an onset at  $\sim 0.05\text{ eV}$  (inset Fig. S13, ESI<sup>†</sup> right panel) with a dependence on  $E_c$  consistent with experiment<sup>34</sup> whereas including all initial  $\nu$ -states for  $\text{O}_2$  and those starting from  $\text{O}_2(\nu > 0)$  again show a decaying probability distribution with increasing  $E_c$ . Because both, initial  $\nu$  and  $j$  are probably “cold”, it is meaningful to consider final  $\text{CO}(\nu' = 17)$  distributions originating from different  $j_{\text{max}}$  values for the parent  $\text{O}_2$  molecule. With decreasing  $j_{\text{max}}$  the  $\text{CO}(\nu' = 17)$  channel opens with increasing values of  $E_c$ . For  $j_{\text{max}}^{\text{O}_2} < 30$ , the onset occurs at 0.05 eV and shifts to  $\sim 0.15\text{ eV}$  for  $j_{\text{max}}^{\text{O}_2} < 10$ , which is consistent with the estimate of 0.188 eV based entirely on energetic arguments above. A temperature of  $T = 300\text{ K}$  corresponds to  $\text{O}_2(j = 12)$  but the corresponding (nonequilibrium) distribution probably extends to higher  $j$ -values. Hence an estimated onset of generating  $\text{CO}(\nu' = 17)$  for  $E_c \in [0.05, 0.10]\text{ eV}$  is expected from the present simulations. This corresponds to a difference of 0.01 eV to 0.06 eV from experiment on a scale of 4 eV, which is an error of 1% at most.



For the deactivation of  $O(^1D)$  to  $O(^3P)$  in the atmosphere early models performed well for the observed data available at that time.<sup>23</sup> Carbon monoxide was categorized as a case that is dominated by the configuration of a critical region where a crossing between the single PESs originating from the  $O(^1D)$  channel cross the triplet PESs leading to  $O(^3P)$ . For the crossing dynamics a Landau-Zener model was assumed. This simple approach lead to a predicted rate of  $8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K which was within the error of experimental measurements of  $7.6$  and  $7.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>14,70</sup> Following this, the deactivation of  $O(^1D)$  by CO was measured<sup>22</sup> and the rate obtained was fit by the expression  $(4.7 \pm 0.9) \times 10^{-11} \exp((126 \pm 33)/RT)$  (with  $E$  in  $\text{cal mole}^{-1}$ ) which yields a rate of  $5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K. Assuming  $\sim 5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the collision rate, this implies a  $\approx 10\%$  efficiency for deactivation of  $O(^1D)$  to  $O(^3P)$  at 300 K. Based on this low efficiency, crossing between the singlet and triplet manifolds are not expected to have a large impact on the formation, exchange or relaxation of the reaction.

As Tully pointed out,<sup>23</sup> deactivation depends on the specific crossing geometry of the PESs; in this case the singlet and triplet surfaces. Fig. S14 and S15 (ESI<sup>†</sup>) show the crossings of the  $^3A$  with the  $^1A$  surfaces on PESs evaluated at the inner (Fig. S14, ESI<sup>†</sup>) and outer (Fig. S14, ESI<sup>†</sup>) turning points for the  $CO(\nu = 0)$  vibration. When starting from the  $CO_A + O_B$  side of the reaction, as was previously mentioned, Fig. 8 shows that the active reactions sample a channel near  $140^\circ$  that brings the outgoing  $O_A$  atom into approximately  $R = 3.5a_0$ . At low temperature, starting from  $CO + O(^3P)$ , it would be possible to cross from any of the  $^3A$  surfaces onto the  $^1A'$  surface to lead to ground state  $CO_2$ . However, in a collisionless environment the complex will still have sufficient energy to return to the  $^1A'$  PES and will have to cross with a  $^3A$  surface to leave as  $O(^3P)$ . This may affect vibrational energy transfer or the exchange reaction and may be the reason for the shifts in the onset seen between the experiment and QCT such as in Fig. 7 at low temperature. Starting from  $CO + O(^1D)$  and traveling along the  $^1A'$  surface crosses all  $^3A$  surfaces while the  $(2)^1A'$  and  $^1A''$  surfaces only cross the repulsive  $(2)^3A''$  surface. At temperatures lower than that required to form  $C(^3P) + O_2$  these trajectories can potentially cross on to the  $^3A$  surfaces and then return to the  $CO + O(^3P)$  state although it would be at high CO vibrational state.

One finding of the present work is the role “gating” plays in the different processes considered here. For one, vibrational relaxation with atom exchange displays gating in the contact time distributions which hints at a time-dependent barrier in the  $[COO]$  collision complex. This is explicitly seen in the barriers for the  $CO_A(^1\Sigma^+) + O_B(^3P) \rightarrow CO_B(^1\Sigma^+) + O_A(^3P)$  atom exchange reaction on the  $^3A'$  PES (Fig. S9, ESI<sup>†</sup>). Depending on the phase of the CO vibration at which the impinging oxygen atom collides with the diatomic molecule, the barrier for formation of the collision complex is either high or low. Such processes are particularly susceptible to zero-point vibrational effects which can not be captured in QCT simulations. Specifically, the vibrational wavefunction does not produce the same spatial

probability distribution at low  $\nu$  as the classical trajectory. This results in differences in sampling times for when the gate is open *versus* closed. The rates from QCT simulations should, therefore, underestimate the true rates, in particular at low temperatures. This is indeed found for vibrational relaxation, see Fig. 7 and for the atom exchange reaction S7 (ESI<sup>†</sup>). As the vibrational relaxation rates include both, processes with and without atom exchange, and the CO vibration-dependent barriers only affect trajectories with atom exchange, it is conceivable that vibrational relaxation without atom exchange is not affected by these effects.

Including zero-point effects is likely to improve the comparison between calculations and experiments. Furthermore, nonadiabatic effects may further improve comparison with experiment, in particular for the processes leading from  $CO_2$  to the  $O + CO$  asymptotes. Analysis of vibrational relaxation demonstrates that depending on the process considered (with or without reaction), different parts of the fully-dimensional PES are sampled. This is also true for reactions at low (15 K) and higher (1000 K) temperatures, respectively. Together with suitable information from experiment the underlying PESs could be further improved from techniques such as morphing<sup>71,72</sup> or Bayesian inference.<sup>73</sup>

The wave function analysis for the SA-CASSCF reference of the  $CO_2 \rightarrow CO + O$  dissociation channel, rationalizing the topography of this region of the PESs. No avoided crossings or conical intersections occur for the five lowest states along the dissociation for the bent  $CO_2$  geometry. The wave function analysis shows that the four lowest excited states of  $CO_2$  undergo a Jahn-Teller splitting caused by the splitting of the  $\pi$  system frontier orbitals upon bending of  $CO_2$ . The five lowest electronic states arise then from different configuration state functions of four electrons in three frontier orbitals and rationalize the relative energy ordering of these states along the dissociation path for the bent geometry of  $CO_2$ .

In conclusion, the present work provides a comprehensive characterization of the energetics and dynamics of the reactive  $[COO]$  system involving the lowest five electronic states. Many findings provide good agreement between simulations and experiments but it is also found that disagreements can be traced back to neglecting quantum mechanical effects at low temperatures. Additional experiments for this important system will provide a more complete understanding of the reactions involving both asymptotes.

## Data availability

All information necessary to construct the potential energy surfaces is available at <https://github.com/MMunibas/CO2-PESs>.

## Conflicts of interest

There are no conflicts to declare.



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