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Classical trajectory study of the HOCO system using a new interpolated ab initio potential energy surface

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Abstract

A new ab initio ground state potential energy surface (PES) for the $OH + CO \rightarrow H + CO_2$ reaction is presented. A modified Shepard interpolation method has been used to construct the PES, based on electronic structure calculations on a set of data points generated iteratively. Quasiclassical trajectory calculations yield cross-sections for the $OH + CO$ reaction that are much smaller than found experimentally, but the energy dependence of the cross-sections for the reverse $H + CO_2$ reaction is in qualitative agreement with experiment, thanks to the incorporation of a *trans*-$H \cdot OCO$ barrier in the PES.
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1. Introduction

Recent years have witnessed an increasing interest in the $OH + CO \rightarrow H + CO_2$ reaction and its reverse. The fundamental and practical importance of the system explains the large number of studies devoted to the elucidation of its kinetics and dynamics. Thus, the reaction of the OH radical with the CO molecule is known to be relevant to the chemistry of the troposphere [1] and of combustion processes [2]. Furthermore, this reaction has become the prototypical four-atom reaction proceeding with formation of a complex, which has been characterised in the gas phase [3].

Properties of the $OH + CO$ reaction derived from experiment include rate constants in a large temperature and pressure range [4,5] and total cross-sections [6]. For the $H + CO_2$ reaction, photolysis experiments [7–9] have provided total and differential cross-sections as well as detailed properties of the diatomic products resulting from the reactive event.

On the theoretical side, a considerable effort has been invested in obtaining an accurate PES for the system. Following the many-body expansion PES for the

ground electronic state of the system reported by Schatz, Fitzcharles and Harding (SFH) in 1987 [10], several improved versions based on more accurate electronic structure calculations have been made available. These include the PESs of Kudla, Schatz and Wagner (KSW) [11], Bradley and Schatz (BS) [12], Yu, Muckerman and Sears (YMS) [13], and Lakin, Troya, Schatz and Harding (LTSH) [14]. In this study, comparisons will be made with the most recent and probably most accurate PES reported to date, i.e., the LTSH PES. Kinetic modelling studies [4,5,15] have shown that an accurate description of the entrance and the exit channel regions of the $OH + CO$ reaction are crucial to reproducing the experimental temperature and pressure dependence of the rate constants.

According to the most recent ab initio information available [13,16,17], there are two transitions states (TSs) in the entrance channel of the potential. These two transition states (*trans*- and *cis*-$HO \cdot CO$) connect the $OH + CO$ entrance channel reactants to the corresponding tightly bound HOCO complexes. In turn, the *cis*-HOCO complex is connected to a transition state (the *cis*-$H \cdot OCO$ TS) in the exit channel, leading to $H + CO_2$ products. The lowest entrance and exit channel adiabatic barrier heights (for *trans*-$HO \cdot CO$ and *cis*-$H \cdot OCO$, respectively), which include zero-point energy

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(ZPE) differences, are predicted to be around 1 kcal mol^{-1}, with passage through the *cis*-H·OCO TS being the rate-determining step.

The existence and properties of the *trans*-H·OCO TS, which connects the *trans*-HOCO complex to H + CO$_2$, have received very limited attention [18]. This feature is present in most of the previous PESs due to the analytical many-body expansion, but no attempt has been made to refine its properties based on accurate electronic structure data. The need to improve the exit channel region of the potential has been suggested by the very recent 6D time-dependent wave packet calculations on the LTSH PES [19]. In that study, thermal rate constants for OH + CO were estimated and found to be much lower than experiment at temperatures below 500 K. The need to improve this region is further emphasised by the inability of the LTSH PES to correctly predict the qualitative energy dependence of the H + CO$_2$ reaction cross-sections, as found recently in QCT calculations [20].

In this Letter, a new ab initio ground state PES for the OH + CO → H + CO$_2$ reaction is presented. The method developed by Collins and coworkers [21–25] based on the modified Shepard interpolation method [26] was used to construct the PES, which we shall refer to as the Leiden PES. Cross-sections were obtained for the OH + CO reaction on the new PES by using the QCT method, and were compared with those obtained on the LTSH PES in an extended collision energy range (0.1–1.13 eV). Furthermore, cross-sections were also calculated for H + CO$_2$, even though no data points were generated for this reaction. For both reactions, important differences were found between our results and those derived from the LTSH PES. We believe that these differences are mainly due to the *trans*-H·OCO barrier in our new PES being much higher than in all previous PESs.

2. Method

2.1. Iterative construction of the PES using modified Shepard interpolation

The construction of the PES is based on the modified Shepard interpolation method [26]. The method has been described in detail and applied to a number of gas phase and gas-surface reactions by Collins and coworkers [21–25,27,28]. In this work, the method has been used as it is implemented into the GROW package, although with some modifications (see below). In the application of the method to the HOCO system, an arbitrary point in configuration space is represented by a set of $N \times (N-1)/2 = 6$ inverse interatomic distances $\xi = (\xi_1, \ldots, \xi_6)$, where N is the number of atoms of the system.

Given a set of reference ab initio data points, the potential energy in a point ξ situated close to one of the data points, e.g., $\xi(i)$, can be expressed as a second-order Taylor expansion $T_i(\xi)$ relative to $\xi(i)$. In the method of Collins and coworkers, the potential energy at an arbitrary point is therefore expressed as a weighted sum of such Taylor expansions $T_i(\xi)(i = 1, \ldots, N_{\text{data}})$ centred on the data points

$$V(\xi) = \sum_{g \in G} \sum_{i=1}^{N_{\text{data}}} w_{\text{goi}}(\xi) T_{\text{goi}}(\xi), \tag{1}$$

where G is the symmetry group of the system, goi the transformation of data point i by the group operation g into an equivalent point, and w_{goi} the weight given to the original and transformed data points. In this work, a two-part weight function has been used, with the parameters set to $q = 2$ and $p = 12$ [25]. To define the confidence lengths in the weight formula [25], the number of nearest neighbours was chosen as 48 and the error tolerance was taken to be 2×10^{-4}. Each Taylor expansion requires the energy and the first and second derivatives at each data point, which must be provided by electronic structure calculations.

In practice, the points on the PES are generated in an iterative fashion [21–25]. First, an ab initio method is chosen and a reference PES is constructed from a set of data points situated on and around the assumed reaction paths for the reaction. Then, a sufficient number of quasiclassical trajectories to ensure at least a few reactive events are run on this approximate PES. A sample of the configurations visited by both the reactive and non-reactive trajectories is recorded. One or more points are then chosen from this sample according to two criteria: the first criterion is to add a data point which is in the region most frequently visited by the trajectories ('*h*-weight' criterion [21,22]); the second criterion is to add a data point in the region which presents the largest error in the interpolation ('variance sampling' criterion [23]). The chosen point(s) is (are) then added to the potential data set and trajectories are run again. The quality of the PES is controlled by monitoring a relevant dynamical property of the reaction under study, e.g., a reaction probability or cross-section. The process is iterated until the numerical value of the chosen property does not change with the addition of data points to the PES, by more than a predefined maximum value.

2.2. Application to the HOCO system

To compute the necessary energies and their first and second derivatives on the data points for HOCO, a combination of different electronic structure methods was set up (see below). This combination of methods was applied to several points situated on and close to the reaction paths to construct the data set for the initial

PES. Some additional points were added to this set for large separations between the OH and CO diatoms, and between the H atom and the CO_2 molecule. The initial PES contained a total of 242 data points. The iterative construction of the PES was then started by defining microcanonical initial conditions for the quasiclassical trajectories consistent with the rovibrational ground states of the OH and CO diatoms ($OH(v = 0, j = 0) + CO(v = 0, j = 0)$ and was carried out simultaneously at four different collision energies, namely, 0.10, 0.33, 0.56, and 0.80 eV. The trajectories were initiated for a distance between the centres of mass of OH + CO of 15.0 bohr, with zero initial impact parameter (as in, for example [24]). After the collision had taken place, trajectories were stopped once the distance between the centres of mass of OH and CO, or of H and CO_2, was greater than 15.0 bohr. A small time step (0.005 fs) was required to ensure energy conservation of the trajectories to within 0.1% or better, even at the lowest collision energy (0.1 eV).

The approach of constructing the PES at different collision energies of the reactants has been shown to lead to reliable results for other reactions [27,28]. In the process of growing the PES, 100–300 trajectories were run at each collision energy as appropriate to ensure reactive events. Originally, the convergence of the total cross-sections at each of the four collision energies was monitored after addition of every 150 points by running batches of 20 000 trajectories. However, since the cross-sections for the OH + CO reaction were found to be rather low (<0.5 bohr²), up to 80 000 trajectories per collision energy were run starting from a PES that contained 800 points. For a smaller number of points, changes in the cross-sections were still large enough that running such a large number of trajectories was not warranted.

2.3. Ab initio methods

The selection of suitable ab initio methods to compute the PES of the HOCO system deserves a separate account. As stated above, the method of construction of the PES requires not only energies, but also first and second derivatives at the data points. In principle, the most accurate choice would be to use a single very accurate method to obtain all the required ab initio information. However, this procedure was deemed unfeasible due to the large computational expense implied. Instead, the energies of the data points were calculated at the highest ab initio level that was found computationally affordable. On the other hand, 'cheaper' methods were sought to approximate the hypothetical highest-level derivatives as accurately as possible.

The energies of the data points were calculated using the so-called 'Full Coupled-Cluster/Complete Basis Set'

(FCC/CBS) method devised by Yu et al. [13]. In this scheme, the final energy is expressed as follows:

$$
\begin{aligned}
E_{\text{FCC/CBS}} = {} & E_{\text{UCCSD(T)/cc–pVQZ}} \\
& + \tfrac{27}{37}x\big[E_{\text{UCCSD(T)/cc–pVQZ}} - E_{\text{UCCSD(T)/cc–pVTZ}}\big] \\
& + \tfrac{1}{5}E^{\text{T}}_{\text{UCCSD(T)/cc–pVTZ}},
\end{aligned} \tag{2}
$$

where $E^{\text{T}}_{\text{UCCSD(T)/cc–pVTZ}}$ is the perturbation energy of the connected triple excitations calculated at the UCCSD(T)/cc-pVTZ level. In Eq. (2), the second term on the right-hand side is an estimate of the correction to the UCCSD(T)/cc-pVQZ energy required to approach the complete basis set limit, and the third term represents a CI truncation error correction [13]. The molecular orbitals (MOs) on which the coupled-cluster expansion is based were either restricted open-shell Hartree–Fock (ROHF) orbitals, mainly in the strong interaction region of the potential, or natural orbitals computed for the lowest root of a state-average complete active space self-consistent field (CASSCF) calculation, in the diatom asymptotic region. For the latter, the active space was made up of three electrons distributed in two MOs. The use of the CASSCF method in the long-range OH + CO region was motivated by the presence of two quasi-degenerate electronic states deriving from the doublet Π character of the OH diatom. Use of this method ensures that the MOs taken as a basis for the coupled-cluster expansion correspond to the lower of the two possible roots, and also improves convergence when compared with the ROHF method.

The first and second derivatives with respect to nuclear displacements at the data points were calculated by combining up to three methods: the UCCSD(T)/aug-cc-pVDZ method (numerical derivatives); the modified Perdew–Wang 1-parameter model for kinetics (MPW1K) hybrid Hartree–Fock-density functional (HF-DF) model [29] with the cc-pVTZ basis set (analytical derivatives); and the LTSH PES (numerical derivatives). The configuration space was divided into three regions (A, B and C) according to the value of the separation between the centres of mass of the OH and CO diatoms (R), and different methods were used in each region. Details are given in Table 1. A switching function was introduced to ensure a smooth transition between regions (A) and (B)

$$
\text{Sw}(R) = 0.5 \times (1 + \tanh(\gamma(R - R^*))). \tag{3}
$$

In Eq. (3) the parameters γ and R^* were given the values 9.0 bohr^{-1} and 5.5 bohr, respectively. The switch was implemented in the iterative construction of the PES as follows: whenever a point chosen during the growing process fulfilled the condition $5.3 < R < 5.7$ bohr, first and second derivatives were calculated with the two methods appropriate to regions (A) and (B). These two results were then combined with coefficients determined by the switching function (see Table 1). Note that no

Table 1
Ab initio methods used to construct the Leiden potential surface

Region	Definition	Energy	First and second derivatives
(A)	$5.5 < R < 15.0$	FCC/CBS (CASSCF(3,2) MOs)	LTSH PES
(B)	$3.8 < R < 5.5$	FCC/CBS (CASSCF(3,2) MOs)	$70\% \times$ MPW1K/cc-pVTZ $+ 30\% \times$ UCCSD(T)/aug-cc-pVDZ (CASSCF(3,2) MOs)
(A)–(B)	$5.3 < R < 5.7$	FCC/CBS (CASSCF(3,2) MOs)	$Sw \times (A) + (1-Sw) \times (B)$
(C)	$R < 3.8$	FCC/CBS (ROHF MOs)	$70\% \times$ MPW1K/cc-pVTZ $+ 30\% \times$ UCCSD(T)/aug-cc-pVDZ (ROHF MOs)

'MOs' stands for molecular orbitals, and 'Sw' stands for switching function (see text, Eq. (3)).

correction is required for the energies since they are calculated in the same way in regions (A) and (B).

There are a few points worthy of note. The particular combination coefficients for the UCCSD(T) and MPW1K methods in the derivative calculations (0.3 and 0.7, respectively, see Table 1) was chosen because this linear combination reproduces the FCC/CBS energies at all the stationary points of the PES with a maximum error of 1 kcal mol^{-1}. Note also that no switching function was defined between regions (B) and (C), even though the UCCSD(T) calculations are based on different MOs in these regions. We believe that this choice does not introduce significant numerical errors in the interpolated PES, as will be explained below.

The use of the LTSH PES for the long-range OH + CO numerical derivatives was motivated by the tight convergence criterion required for the wave functions (10^{-10}). In that region, this criterion could not be met by the single-reference MPW1K method. Note that at long OH–CO distances, the LTSH PES is an accurate fit to UCCSD(T)/aug-cc-pVDZ calculations, and the energies of the stationary points at this level of calculation only differ from the FCC/CBS values by a few tenths of a kcal per mole.

All the coupled-cluster calculations were performed with the MOLPRO code [30], while for the hybrid HF-DF calculations use was made of GAUSSIAN'98 [31]. Numerical derivatives in the long-range OH + CO region were evaluated from the LTSH PES code. Several modifications were introduced into the GROW script to be able to use both electronic structure packages, as well as the LTSH PES derivatives and the switching function, during the iterative construction of the PES.

2.4. Evaluation of stationary points and trajectory calculations

The stationary points on the Leiden PES have been located and characterised using the algorithms implemented in the POLYRATE code [32]. The QCT calculations used to construct the PES, to monitor the convergence of the cross-sections, and to obtain final results for non-rotating reactants, were carried out using the methods implemented by Collins and coworkers [21–25]. Initial conditions for rotating OH and CO

diatoms were obtained using the VENUS'96 program [33]. In this case, trajectories were propagated using the methods mentioned above.

3. Results and discussion

As explained above, the convergence of the total cross-section for the OH + CO reaction was checked against the number of data points in the PES. To this aim, 80 000 trajectories were run for each collision energy after addition of every 150 data points, starting with a potential file that contained 800 points. The maximum impact parameter was set to 4.5 bohr for collision energies equal to 0.1, 0.33, and 0.56 eV, and to 4.0 bohr for a collision energy of 0.80 eV. The initial conditions for the trajectories correspond to ground rovibrational states of the reagents. The results are shown in Fig. 1. For a potential file containing 950 data points the calculated cross-section for 0.80 eV is outside the two standard deviation interval of the previous (800 data points) potential file. Likewise, the cross-section for 1100 data points and 0.33 eV differs from the corresponding cross-section for 950 points by more than the
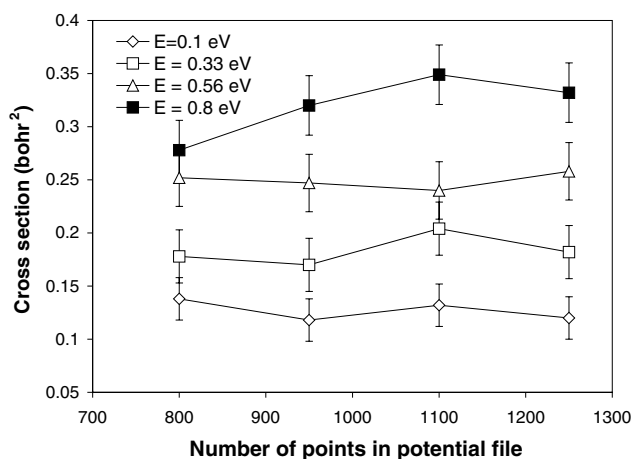

Fig. 1. Convergence test for the growing interpolated Leiden PES. Cross-sections for the OH($v = 0, j = 0$) + CO($v = 0, j = 0$) reaction are shown as a function of the number of points in the potential file. The collision energies are as indicated in the legend, and the error bars correspond to two standard deviations (95% confidence interval).

allowed confidence interval. Only for the potential file of 1250 points are the four values of the cross-section inside the confidence intervals of the previous 1100-point potential file. Note that these confidence intervals represent about 10–15% of the absolute values of the cross-section. Therefore, we conclude that, using 1250 points, the iterative construction procedure has provided a PES from which cross-sections for the OH + CO reaction can be obtained that are converged to within 15%, for collision energies between 0.1 and 0.8 eV. The PES containing 1250 points was chosen to be our new PES and will be used in all subsequent calculations. Henceforth we will call this new potential energy surface the Leiden PES.

The properties of the stationary points on the Leiden PES are shown in Table 2. The relative energies, structures and frequencies are in close agreement with the most recent ab initio studies [13,16,17]. For the sake of comparison, in this work ab initio structures and frequencies of the stationary points were obtained at the UCCSD(T)/cc-pVTZ level. Ab initio energies were then obtained at the FCC/CBS level on the optimised structures. For the stationary points on the Leiden PES, energies relative to OH + CO agree with ab initio FCC/CBS energies within 1 kcal mol^{-1}, and distances and angles of the stationary points typically differ by 0.01–0.02 Å and 2–3°, respectively, from the UCCSD(T)/cc-pVTZ values. With a few exceptions, frequencies and ZPEs also show a good agreement with UCCSD(T)/cc-pVTZ values, with differences of the order of 5–10%. Hence, the modified Shepard interpolation is able to reproduce the ab initio information described above with high accuracy, even though several methods have been used to construct the PES.

Some properties derived from the stationary points on the Leiden PES can be compared with experiment. In what follows, all the energies are ZPE-corrected. The exoergicity of the OH + CO reaction, 24.6 kcal mol^{-1}, compares very well with the experimental value of 24.3 kcal mol^{-1} [3]. The *trans*-HO · CO and *cis*-H · OCO barrier heights of 1.0 and 1.2 kcal mol^{-1}, respectively, are also in good agreement with estimates of the overall reaction barrier from kinetic modelling studies (0.5–2.0 kcal mol^{-1} [4,5,15]). The distance between the centres of mass of the diatoms in the OH · CO minimum ($R = 4.45$ Å), and its binding energy (E_b) with respect to OH + CO (-0.3 kcal mol^{-1}), compare reasonably well with experiment ($R = 3.94$ Å and $-1.2 \leqslant E_b \leqslant 0.0$ kcal mol^{-1}, respectively [17]). Finally, the depths of the *cis*- and the *trans*-HOCO wells, 21.3 and 24.3 kcal mol^{-1}, respectively, are consistent with the experimental upper limit of 27.8 kcal mol^{-1} for the HOCO complex [3].

An important feature of the Leiden PES is the high barrier associated with the *trans*-H · OCO TS, connecting directly the *trans*-HOCO minimum to products, H + CO$_2$. All the previous PESs show a relatively low-

Table 2
Properties of the stationary points found on the interpolated HOCO potential energy surface[a]

Stationary point	Energy[b]	r_{OH} (Å)	r_{OC} (Å)	r_{CO} (Å)	∠HOC (°)	∠OCO (°)	τHOCO[c] (°)	Frequencies (cm^{-1})
OH + CO	0.0(0.0)	0.9668		1.1228				3811.0, 2245.5
trans-HO–CO (TS)	−0.5(1.0)	0.9661	2.1060	1.1265	94.4	123.1	180.0	3843.9, 2253.5, 602.5, 204.4, 197.6, 142.0 i
cis-HO–CO (TS)	2.9(4.0)	0.9683	2.0151	1.1295	91.4	122.2	0.0	3803.7, 2183.5, 710.4, 157.5, 106.3i, 287.1i
OH–CO (min)	−1.6(−0.3)	0.9660	3.8632	1.1227	0.0	180.0		3856.1, 2262.2, 227.4, 225.5(2), 102.0(2)
OH–OC (min)	−0.9(0.3)	0.9664	4.9211	1.1227	0.0	0.0		3857.4, 2265.2, 234.0, 190.7(2), 84.0(2)
trans-HOCO (min)	−29.9(−24.3)	0.9601	1.3395	1.1734	108.0	127.3	180.0	3857.6, 2041.8, 1610.5, 1182.3, 719.6, 541.2
cis–trans-HOCO (TS)	−20.4(−16.7)	0.9619	1.3523	1.1721	109.7	129.6	87.2	3875.7, 1961.9, 1153.8, 1040.1, 668.9, 617.8i
cis-HOCO (min)	−28.4(−21.3)	0.9668	1.3307	1.1790	108.3	130.4	0.0	4054.7, 2051.3, 1999.2, 1512.0, 802.9, 587.4
trans-H-OCO (TS)	23.4(22.4)	1.2344	1.2027	1.1739	116.7	156.8	180.0	2259.3, 1313.4, 1021.5, 539.8, 224.9, 3765.3i
cis-H-OCO (TS)	1.5(1.2)	1.3363	1.2023	1.1621	116.8	157.9	0.0	2259.1, 1394.6, 992.2, 673.4, 562.1, 1970.3i
trans-HOCO–HCO$_2$ (TS)	8.3(9.1)	1.2468	1.2853	1.1697	61.6	144.6	180.0	2233.2, 1926.0, 1202.3, 655.7, 596.6, 1781.4i
HCO$_2$ (min)	−13.6(−10.5)	1.8728	1.2925	1.1916	36.1	134.6	180.0	2674.0, 1867.4, 1240.5, 1045.5, 966.5, 447.6
H–CO$_2$ (TS)	−9.5(−10.1)	2.0450	1.1808	1.1808	45.1	159.4	180.0	2209.4, 1395.1, 815.5, 736.8, 486.5, 1101.5i
H–OCO (min)	−23.6(−24.6)	3.866	1.1564	1.1563	90.0	180.0	180.0	2456.3, 1402.6, 696.6, 694.9, 97.9, 18.3
H + CO$_2$	−23.5(−24.6)		1.1563	1.1563		180.0	180.0	2456.0, 1403.0, 697.5(2)

[a] Energies given in kcal mol^{-1} with respect to the reference OH + CO asymptote energy of −188.895133 au. 'min' Stands for minimum.
[b] In parentheses, zero-point corrected energy difference with respect to the OH + CO asymptote.
[c] H–O–C–O′ dihedral angle.

lying region around the *trans*-configuration in the exit channel. The ab initio methods used in this study show consistently a high *trans*-H·OCO barrier. The MPW1K/cc-pVTZ functional predicts a barrier of 18.2 kcal mol^{-1}, while the UCCSD(T)/cc-pVTZ method predicts a barrier of 27.6 kcal mol^{-1}. As will be shown below, the presence of this barrier has a large effect on the dynamics of the OH + CO → H + CO$_2$ reaction and its reverse. To our knowledge, only one previous ab initio study has reported on the *trans*-H·OCO TS [18]. In that study, the multiconfigurational self-consistent field (MCSCF) and multi-reference CI (MRD-CI) methods with a double-ζ basis set were used to find a much larger barrier for the *trans*-H·OCO TS than for the *cis*-H·OCO TS. At the MRD-CI level, the reported values are 38.0 and 18.4 kcal mol^{-1}, respectively. Due to the relatively low level of correlation used, these values highly overestimate those reported here and in recent ab initio studies. However, they do show that the *trans*-H·OCO TS is a feature of the HOCO PES and that its energy is much higher than that of *cis*-H·OCO TS.

In Fig. 2, the distribution of data points in the Leiden PES is shown as a function of the distance between the centres of mass of the OH and CO diatoms (R). For reference, the *trans*-HO·CO TS has $R = 4.8$ bohr, and the *cis*-H·OCO TS has $R = 3.5$ bohr (see Table 2). Most of the data points concentrate on the strong interaction region of the potential, with values of R between 3.2 and 4.0 bohr. Notice that the region near $R = 3.8$ bohr is the limit between regions (B) and (C) of the potential (see Table 1). The average difference between the FCC/CBS energies from methods (B) and (C) at points with R near 3.8 bohr is about 0.3 kcal mol^{-1}. This energy difference does not seem to cause a significant error in the interpolated PES, even though a switching function was not introduced. This observation is supported by the absence of a particular accumulation of points near
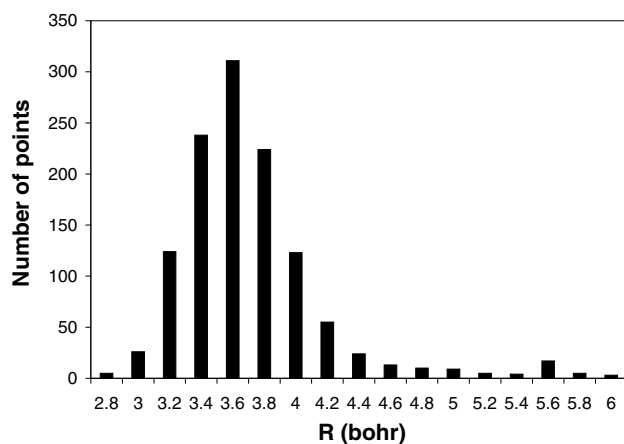
$R = 3.8$ bohr. Such an accumulation would be expected in the iterative construction of the PES if numerical errors were important, since the addition of new points to the potential data file is partly based on the accuracy of the PES in a particular region ('variance sampling' criterion [23], see above).

Cross-sections obtained for the OH + CO reaction with the Leiden PES are presented in Fig. 3. Cross-sections derived from the LTSH PES are also shown. A striking observation is that the Leiden PES yields much smaller cross-sections than the LTSH PES. The difference is about a factor of three to four at collision energies between 0.1 and 0.8 eV. This substantial difference is most likely caused by the large *trans*-H·OCO barrier (∼1 eV) in the Leiden PES, that shuts off reaction at all collision energies. This barrier is slightly less than 0.1 eV high in the LTSH PES, comparable with the *cis*-H·OCO barrier. To show that the entrance channel of the reaction cannot be responsible for this different behaviour, the probability of crossing the entrance channel region was monitored for both the LTSH and the Leiden PES. The probabilities were found to differ by at most 20% for collision energies between 0.1 and 0.8 eV. This lends further support to the view that the *trans*-H·OCO TS is responsible for the reduction in the reactivity of the Leiden PES.
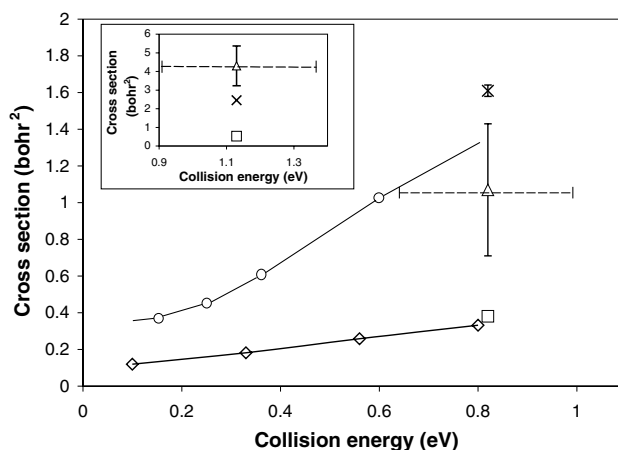

Fig. 3. Cross-sections for the OH + CO reaction. Results for the OH($v = 0, j = 0$) + CO($v = 0, j = 0$) reaction at different collision energies and using the LTSH (circles, [14]), and the Leiden PES (diamonds). Lines are merely a visual aid. At 0.82 and 1.13 eV (see inset), results for the OH($v = 0, j_{OH}$) + CO($v = 0, j = 7$) reaction are presented for the LTSH PES (crosses) and for the Leiden PES (squares), for $j_{OH} = 7$ (0.82 eV) and 12 (1.13 eV), respectively. For both collision energies, triangles represent the experimentally measured cross-sections [6] and the initial rovibrational states of reactants in the calculations were selected to approximate the conditions of the experiments (CO($T = 300$ K), $\langle j_{OH} \rangle = 7$ for 0.82 eV and 12 for 1.13 eV). Dashed horizontal lines represent the width (FWHM) of the experimental centre-of-mass collision energy distribution. Theoretical error bars correspond to one standard deviation, but they are not shown if their size is smaller than the symbol size.

Fig. 2. Histogram showing the distribution of the data points on which the Leiden PES is based over R, i.e., the distance between the centres of mass of the OH and CO diatoms.

In Fig. 3, a comparison with the available experimental cross-sections at 0.82 and 1.13 eV [6] is also provided. The initial conditions of the reactants were selected in such a way as to make a meaningful comparison to the experiments possible. At 0.82 eV, the Leiden PES yields a value that is about 60% lower than the experiment, while the LTSH PES overestimates the experiment by about the same percentage. At 1.13 eV, both PESs are far below the experimental value, by a factor of eight and two for the Leiden and LTSH PESs, respectively. Note that at 1.13 eV the Leiden PES is not expected to be very reliable, since no data points were generated around that energy. However, even when allowing for the large experimental error bars, neither one of the PESs is capable of reproducing the experimental cross-sections. Previous experiments for a collision energy of 1.32 eV [34] gave a value for the cross-section of 68 ± 36 bohr^2, much larger than the result of a QCT simulation using the KSW PES (3.9 ± 0.4 bohr^2) [34]. In that same QCT study, the outcome of the experiment at 1.32 eV was criticised as being physically unreasonable. It was also shown that QCT results on the same KSW PES were in good agreement with the experiment at 0.82 eV, and reasonably close to it at 1.13 eV [6]. However, the recent QCT study on OH + CO, mainly focused on the LTSH PES [14], has revealed that the KSW PES gives much larger cross-sections than the more accurate LTSH PES up to collision energies of 0.9 eV. Furthermore, this result corresponds to a total energy conservation in the trajectories of 5%. When a more strict energy conservation criterion is imposed (e.g., 1%), KSW cross-sections diminish considerably [14]. Thus, the agreement with the experiment would tend to worsen for these corrected cross-sections for the KSW PES.

In conclusion, a word of caution seems appropriate also regarding the validity of the more recent cross-sections at 0.82 and 1.13 eV [6], to which we are comparing in this study. In particular, the evidence presented above suggests that the available experimental cross-sections for OH + CO are probably too large.

Cross-sections for the reverse reaction, H + CO$_2$, with the CO$_2$ molecule in its ground rovibrational state, are presented in Fig. 4. A maximum impact parameter of 3.5 bohr was used for all the calculations. The results are compared with those obtained with the LTSH PES [20] and in experiments [7,8]. Interestingly, the Leiden PES is capable of predicting the cross-sections quantitatively up to a collision energy of about 1.8 eV, and qualitatively for larger collision energies. The agreement found for the Leiden PES up to 1.8 eV is remarkable, since all data points were generated for the OH + CO reaction. As shown in Fig. 4, the LTSH PES fails to describe qualitatively the dependence of the cross-section on collision energy. Instead, it largely overestimates the experimental cross-sections at collision energies up to 2.2 eV, and it shows a mild decrease from 1.8 to 2.5 eV.
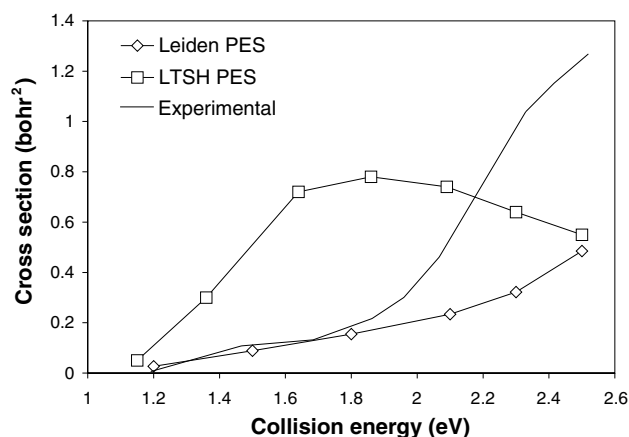

Fig. 4. Cross-sections for the H + CO$_2$ reaction. In the theoretical simulations, the LTSH and Leiden PESs are employed (see legend), with the CO$_2$ molecule kept in its ground rovibrational state. LTSH results are taken from [20]. Experimental data derive from the experiments in [7,8]. Error bars on the theoretical results are not shown, since their size is smaller than the symbols' size. Lines are merely a visual aid.

This different behaviour can be understood by considering the height of the barriers in these two PESs, measured from H + CO$_2$. The Leiden PES presents three barriers in the entrance channel of the H + CO$_2$ reaction: a *cis*-H · OCO barrier (1.1 eV), a *trans*-HOCO–HCO$_2$ barrier (1.4 eV), and a *trans*-H · OCO barrier (2.0 eV), see Table 2. This is consistent with the activated behaviour seen at all collision energies, and in particular, at energies close to and larger than 2.0 eV. For the LTSH PES, the *trans*-H · OCO barrier is only about 1.1 eV high, the largest barrier being 1.3–1.4 eV for the *trans*-HOCO–HCO$_2$ TS. The absence of a barrier at energies higher than 1.4 eV could explain why the LTSH cross-sections are too large up to about 2.0 eV, and why they do not increase with energy in the collision energy range 1.8–2.5 eV.

All the cross-section calculations in this work have made use of the QCT method. In recent work on the OH + CO reaction [19,35], it has been shown that the QCT method has a tendency to overestimate exact 6D quantum dynamics reaction probabilities for total angular momentum $J = 0$, both when using the LTSH PES [19] and the BS PES [35]. This tendency was attributed to a ZPE conservation problem and found to be more important the lower the collision energy is. For the BS PES, QCT and quantum results tend to agree at high ($\sim$0.8 eV) collision energies [35]. At low collision energies, tunnelling through the *cis*-H · OCO TS barrier could also be relevant. In previous PESs, the imaginary frequency of this TS is probably too small, leading to low tunnelling probabilities. In the Leiden PES, the imaginary frequency is larger and in-line with ab initio values (see Table 2), which should lead to larger tunnelling probabilities. Therefore, at low collision energies

a quantum dynamics method is probably required to obtain meaningful cross-sections for the Leiden PES. The above suggests that QCT cross-sections for the Leiden PES are probably reliable at high energies, whereas their accuracy at low energies remains to be established.

In the most recent QCT study on the $H + CO_2$ reaction [20], the ZPE conservation problem was also found to be relevant. In that study, an analysis was performed of the effect on the dynamics of keeping only those trajectories for which the vibrational energy of either or both of the products, $OH + CO$, is at least the ZPE. From this analysis, the authors concluded that the most reliable results are obtained when no constraints are applied to the ZPEs. On the other hand, due to the higher collision energies involved QCT results are expected to compare better with the quantum dynamics results for the $H + CO_2$ reaction, than for the $OH + CO$ reaction. These considerations lead us to believe that the accuracy of our ZPE-unconstrained QCT results for the $H + CO_2$ reaction are essentially only limited by the accuracy of the Leiden PES.

4. Conclusions

In this Letter, a new, interpolated PES for the HOCO system, based on new high-level ab initio calculations and information from the LTSH PES at long range, has been presented and coined the Leiden PES. Quasiclassical trajectory cross-sections for the $OH + CO$ reaction were found to be 3–5 times smaller than those for the LTSH PES, for collision energies between 0.1 and 1.13 eV. The lower cross-sections obtained with the Leiden PES are most likely due to the presence of a much higher *trans*-H · OCO barrier in the exit channel of the reaction than has heretofore been assumed. This conclusion is supported by the small difference (20%) between the Leiden and LTSH PESs regarding the probability of crossing the entrance channel region of the $OH + CO$ reaction. Furthermore, the presence of a large *trans*-H · OCO barrier is consistently predicted by the different electronic structure methods used here.

Interestingly, the experimental cross-sections available for the $OH + CO$ reaction were not reproduced with either one of the PESs used in this study. The Leiden PES represents an improvement of the exit channel of the $OH + CO$ reaction, and it is of comparable accuracy to the LTSH PES in the entrance channel. We conclude that the use of the LTSH PES will lead to cross-sections that are probably too large for the ground state PES for the $OH + CO$ reaction at not too low collision energies (i.e., for $E_i > 0.1$ eV, where the *trans*-H · OCO TS can be crossed on the LTSH PES). On the other hand, we expect the Leiden PES to predict reliably the $OH + CO$

cross-section at 0.82 eV, assuming that the excited state PES of the system does not participate significantly at that collision energy. All this evidence casts some doubt on the accuracy of the experimental cross-sections, which appear to be too large, as discussed more fully in Section 3.

Even though no points were included in the PES for initial conditions corresponding to the $H + CO_2$ reaction, QCT cross-sections for this reaction are in reasonable agreement with experiment. In particular, the monotonous increase of the cross-section in the full range of collision energies investigated (1.2–2.5 eV) is described quantitatively up to 1.8 eV, and qualitatively for collision energies larger than 1.8 eV. This increase can be attributed to the correct description and incorporation of potential barriers for the $H + CO_2$ reaction up to 2.0 eV, in particular of the *trans*-H · OCO TS barrier, in the Leiden PES.

We are planning to generate a new version of our PES that describes the higher energy regions of the PES more accurately than the current version. In particular, initial conditions for both direct and reverse reactions will be included in the iterative growing process. These extensions are expected to lead to improvements in the cross-sections for the $H + CO_2$ reaction, and in cross-sections for the $OH + CO$ reaction at collision energies higher than 0.8 eV.

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