Calculations of quantum tunnelling rates for muonium reactions with methane, ethane and propane

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Thermal rate constants for Mu + CH₄, Mu + C₂H₆ and Mu + C₃H₈ and their equivalent reactions with H were evaluated with ab initio instanton rate theory. The potential-energy surfaces are fitted using Gaussian process regression to high-level electronic-structure calculations evaluated around the tunnelling pathway. This method was able to successfully reproduce various experimental measurements for the rate constant of these reactions. However, it was not able to reproduce the faster-than-expected rate of Mu + C₃H₈ at 300 K reported by Fleming et al. [Phys. Chem. Chem. Phys., 2015, 17, 19901 and Phys. Chem. Chem. Phys., 2020, 22, 6326]. Analysis of our results indicates that the kinetic isotope effect at this temperature is not significantly influenced by quantum tunnelling. We consider many possible factors for the discrepancy between theory and experiment but conclude that in each case, the instanton approximation is unlikely to be the cause of the error. This is in part based on the good agreement we find between the instanton predictions and new multiconfigurational time-dependent Hartee (MCTDH) calculations for Mu + CH₄ using the same potential-energy surface. Further experiments will therefore be needed to resolve this issue.

1 Introduction

Kinetic isotope effects (KIEs) are a useful probe of the mechanism of chemical reactions. Comparing experimental results and theoretical predictions can also provide a stress-test for the accuracy of potential-energy surfaces (PESs) and various approximations to quantum dynamics.¹⁻¹³ Muonium (Mu = μ⁺e⁻) is an exotic isotope of hydrogen, with a mass about 9 times smaller than H.¹⁴ Due to this very light mass, comparison of the rates of H + Y reactions with Mu + Y (where Y is a member of the family of alkanes: CH₄, C₂H₆, C₃H₈, etc.) are expected to result in strong kinetic isotope effects.

Experiments on Mu + CH₄ and Mu + C₂H₆ show inverse kinetic isotope effects which become more pronounced with decreasing temperature.¹⁵⁻¹⁶ If Mu + C₃H₈ followed this same behaviour, one would expect the rate to be on the order of 1000 less than the reaction with H at 300 K. However, experimental investigations of the Mu + C₃H₈ reaction by Fleming et al.¹⁷ reveal an anomalous KIE at 300 K, wherein the rate is measured to be almost as fast as that of H + C₃H₈. The experiments were recently repeated using a more sensitive technique¹⁸ which confirmed the result at 300 K and provided further data at temperatures up to 435 K, which also demonstrated unexpected KIEs. Similar behaviour was also seen for Mu + n-C₄H₁₀, although data is less reliable for this reaction and we will thus concentrate on the Mu + C₃H₈ case. It was proposed that the rates of the reactions with muonium are considerably sped-up due to tunnelling effects, and it is one aim of this work to test this suggestion.

We first perform transition-state theory (TST) calculations using high-level electronic-structure calculations based on coupled-cluster theory with explicit correlation.¹⁹ We show that these reproduce the high-temperature (T ≥ 500 K) experimental rates (where available) for all H + Y reactions as well as Mu + CH₄ and Mu + C₂H₆ and hence the observed KIEs for these two reactions. Analysis of the TST formula shows that these KIEs are mostly due to zero-point energy corrections of the effective barrier height and to a lesser extent due to minor changes in the translational and rotational partition functions.

In order to correctly predict the reaction rate constant for these reactions at low temperature (T ≤ 300 K), a rate theory is required which takes into account quantum tunnelling. We apply the ring-polymer instanton approach,²⁰⁻²⁴ which is a form of semiclassical transition-state theory.²⁵⁻²⁶ It has been successfully applied to study quantum tunnelling in a wide variety of chemical processes.²⁷⁻³⁹

The instanton is defined as the optimal tunnelling pathway which traverses the barrier region. This pathway is found using
2 Methods

In this section, we outline our approach to predicting reaction rates from first principles at both high and low temperatures. The results of the low-temperature rates are presented and discussed in Section 3.

2.1 Description of the reactions

The bimolecular reactions to be studied are (where X is H or Mu):

\[
\begin{align*}
X^* + CH_4 & \rightarrow XH + CH_3^* \\
X^* + C_2H_6 & \rightarrow XH + C_2H_5^* \\
X^* + C_3H_8 & \rightarrow XH + C_3H_7^* .
\end{align*}
\]

In each case, the reaction is assumed to follow a simple mechanism in which a hydrogen atom is abstracted from the alkane by an incoming radical atom. For X + CH₄ there are four equivalent channels and for X + C₂H₆ there are six equivalent channels. However, reaction with C₃H₈ has eight channels of three distinct types corresponding to abstraction of the hydrogens in three different environments as shown in Fig. 1. 
Abstraction from the primary (terminal) C atoms are termed X + n₁-C₃H₈ and X + n₂-C₃H₈, where we differentiate between abstraction of in-plane (i.e., on the same plane as the carbon chain) (n₁) and out-of-plane (n₂) hydrogen atoms respectively. Abstraction from the secondary (middle) C atom is termed X + i-C₃H₈.

The H + CH₄ reaction has been studied extensively and many excellent precalculated PESs exist. In previous work we have computed the rate for this reaction both “on the fly” and using the GPR approach in order to test our implementations. However, in this paper, we utilise the permutationally-invariant polynomial neural network (PIP-NN) PES fitted by Li et al. to UCCSD(T)-F12a/aug-cc-pVTZ calculations. We do this in order to be able to make a direct comparison with the MCTDH results, and we thus perform TST, ring-polymer instanton as well as MCTDH calculations using this same PES. It should be noted that the total rates which we present are calculated for one reaction channel and are then effectively multiplied by 4 to account for the other indistinguishable channels.

We have obtained ab initio instanton rates for the H + C₂H₆ reaction in a previous study using the GPR-aided instanton approach, wherein the training points were based on UCCSD(T)-F12b/cc-pVTZ-F12 calculations. In this work, we employ an equivalent ab initio approach to accurately evaluate rates for Mu + C₂H₆. A typical training dataset included 30-50 potentials and gradients, and 5-10 Hessians evaluated at the coupled-cluster level. Indistinguishability of the reaction channels is accounted for by multiplying the rate for one channel by 6.

Fig. 1 A schematic representation of C₃H₈, where the three distinct channels for the hydrogen abstraction mechanism are identified. These are labelled n₁, n₂ and i.
The GPR-aided instanton method was again utilised to evaluate instanton rates for each of the three channel types in X + C3H8. The training data were obtained from UCCSD(T)-F12b/cc-pVTZ-F12 calculations, including no more than 80 potentials and gradients and 13 Hessians for each channel. All electronic-structure calculations were performed using MOLPRO.55 The choice of basis set for the electronic-structure calculations was based on the findings by the group of Clary,56 where it was shown that CCSD(T)-F12a/cc-pVTZ-F12 and CCSD(T)-F12a/cc-pVDZ-F12 methods both yield similar results. Indistinguishability is accounted for by multiplying the obtained rate by 2, 2 and 4 for the X + i-C3H8, X + n-C3H8 and X + n2-C3H8 channels respectively. These are then summed to obtain the overall X + C3H8 rate.

To ensure that the coupled-cluster methods are reliable for calculating the transition-state energies, we checked the T1 and D1 diagnostics57–59 obtained from MOLPRO calculations to determine the extent of the electronic wavefunction’s multi-reference character. The largest value of T1 was 0.012 (for H + C2H6) and all D1 values were approximately 0.03 or lower. We found similar values for geometries near the transition state which are used for the instanton calculations. According to standard interpretation, there is a strong indication of multi-reference character if T1 > 0.02 and D1 > 0.05.57,58,60 As we are below these limits, we can therefore assume that the coupled-cluster results are reliable, as will also be confirmed by a comparison of high-temperature TST results with experiment.

2.2 Stationary points of the potential-energy surfaces

The most important factor which determines the rate is the barrier height. However, the most important factor for the tunnelling effect is the barrier width, which can be approximately described by the magnitude of the imaginary frequency, ωb, associated with the transition state. The ring-polymer instanton approach is applicable below a certain crossover temperature TC = h/ωb(2πkB).61 This defines the onset of the deep-tunnelling regime, where significant deviations from the TST results are expected.62

The calculated barrier heights (with and without harmonic zero-point energy corrections) and the crossover temperatures for the reactions of interest are presented in Table 1. It can be seen that the effective barrier heights for the Mu + Y reactions are significantly larger than those of H + Y reactions. The difference arises purely from the increase in some of the frequencies of the transition state and is the main reason that Mu + Y rates are expected to be orders of magnitude smaller than H + Y rates.

It can be observed that all Tc values fall between 320 and 340 K, which suggests that instanton theory will be required for the low temperature regime in this study (i.e. 200 to 300 K), but that the high-temperature studies (T ≥ 500 K) are not in the deep-tunnelling regime such that the use of transition-state theory is justified. In each case the crossover temperature is only slightly higher for the Mu reactant because reducing the mass of this atom increases the magnitude of all the frequencies. The effect is very small because the imaginary mode is dominated by the abstracted H atom, not the incoming radical.

It is interesting to note here that the X + i-C3H8 channel has a significantly lower barrier than X + n-C3H8 and X + n2-C3H8. This means that the X + i-C3H8 rate is expected to be the dominant contributor to the overall X + C3H8 rate. This is justified by the fact that the X + i-C3H8 product channel has a more stable radical than X + n-C3H8.63

An analysis of the symmetry point groups64 of the minima and transition state geometries shows that our simple approach for accounting for the degeneracy of the reactions leads to the correct symmetry factor in each case. We also find that each instanton has the same point group symmetry as the equivalent transition state geometry and thus the same symmetry factors are also valid under that theory.

2.3 MCTDH rate constant calculations

Rate constants for the X + CH4 reactions were calculated using the MCTDH approach obtained by employing the quantum transition-state concept65–74 closely following previous work,75–78 and thus only a short summary of the methods is given. Thermal rate constants are obtained from cumulative reaction probabilities and employing J-shifting79 as

$$k(T) = \frac{Q_{\text{rot}}(T)}{2\pi Q_e(T)} \int dE N_{J=0}(E) e^{-E/kT}. \quad (1)$$

Here Qr(T) denotes the partition function of the reactants, Qe(0) is the (classical) rotational partition function at the transition state and the cumulative reaction probability N_{J=0}(E) is computed using flux–flux correlation functions and a thermal flux operator at a reference temperature T0:

$$N_{J=0}(E) = \frac{1}{2} e^{\frac{E}{2kT_0}} \sum_{f_{T_0}} \left( \int \left| f_{T_0} \right|^2 \right)^{\frac{1}{2}} \left( \left| f_{T_0} \right|^2 \right), \quad (2)$$

where f_{T_0} and | f_{T_0} | are the eigenvalues and eigenstates of the thermal flux operator at T0, respectively. As in previous

| Y     | PES       | V\text{\textscript{i}} | V\text{\textscript{i}}(H) | V\text{\textscript{i}}(Mu) | T\text{\textscript{c}}(H) | T\text{\textscript{c}}(Mu) |
|-------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| CH4   | PIP-NN    | 61.41           | 54.79           | 82.46           | 331             | 331             |
| C2H6  | UCCSD(T)-F12b/cc-pVTZ-F12 | 50.03 | 42.31          | 68.75           | 335             | 337             |
| i-C3H8| UCCSD(T)-F12b/cc-pVTZ-F12 | 42.22 | 34.42          | 59.17           | 321             | 325             |
| n-C3H8| UCCSD(T)-F12b/cc-pVDZ-F12 | 53.26 | 45.80          | 71.26           | 329             | 329             |
| n2-C3H8| UCCSD(T)-F12b/cc-pVDZ-F12 | 51.89 | 44.47          | 72.56           | 327             | 328             |

These are then summed to obtain the overall X + C3H8 rate.

Table 1 The bare electronic barrier height, V\text{\textscript{i}}, and zero-point energy corrected barrier height, V\text{\textscript{i}}(X), are given in kJ mol\textsuperscript{-1}, and the cross-over temperatures, T\text{\textscript{c}}(X), in K, for the X + Y reaction (where X is H or Mu), according to the PES used for each system. In the case of an ab initio PES, the prediction is taken directly from the electronic-structure calculation at the transition state optimised at the same level of theory.
work,\textsuperscript{53,80,81} a harmonic extrapolation is used to account for the thermal flux eigenstates which are not treated explicitly, and the imaginary-time propagation is split with the initial thermal flux eigenvalues computed at a higher reference temperature of 2000 K and then propagated in imaginary time to reach the final reference temperature of \(T_0 = 600\) K. The partition functions are calculated as in previous work\textsuperscript{53,80,81} including anharmonic vibrational contributions.\textsuperscript{82} Note that the results were not scaled based on estimates of the barrier height from higher-level electronic-structure calculations (i.e. CCSD(T)) as was done in some previous work to improve the overall accuracy.\textsuperscript{53} The results can therefore be considered as a benchmark rate for the given PES.

The calculations of the thermal flux eigenstates as well as the subsequent imaginary and real time propagation employ the MCTDH approach\textsuperscript{48,83,84} and its multilayer\textsuperscript{85,86} and state-averaged\textsuperscript{89} extensions as well as the multilayer correlation discrete variable representation.\textsuperscript{86–88} For the \(H + CH_4\) reaction, modified transition-state normal-mode coordinates are used.\textsuperscript{90} The dividing surface was located in the modified transition-state normal-mode coordinates system with \(Q_1' = \sin z Q_1 + \cos z Q_4\), with \(z = 18\), at \(Q_1' = 0\) a.u. Converged results are found with 15 pairs of thermal flux eigenstates and a propagation time of 30 fs. The largest basis set employed in the calculations is given in Fig. 2a. For the \(Mu + CH_4\) reaction curvilinear coordinates,\textsuperscript{90} as used in state-selective descriptions of \(H + CH_4\),\textsuperscript{91–93} were employed. The dividing surface was located at \(r = 125.0\) a.u. Converged results are found with 12 pairs of thermal flux eigenstates and a propagation time of 15 fs. The largest basis set employed in the calculations is given in Fig. 2b.

The largest systems that could be treated with MCTDH simulations to date are six-atomic \(X + CH_4\ (X = Mu, H, D or O)\) reactions. Unfavourable scaling of the quantum dynamics simulations, the need for accurate and efficiently evaluated PES and, for many cases, the need for a dedicated curvilinear coordinate system with complicated kinetic energy operators are the biggest challenges to extend these simulations towards larger reactions. Thus, it is not yet possible to calculate benchmark rate constants for the larger systems employed in this work, \textit{i.e.} for \(X + C_3H_8\) or \(X + C_2H_6\).

### 2.4 TST rates in the high-temperature regime

At high temperatures (\(T \gtrsim 500\) K) well above the crossover temperature, tunnelling is not expected to be significant. Thus in this regime, rates were evaluated with Eyring transition-state theory\textsuperscript{94} for the six reactions of interest. The PESs used in each case were described in Section 2.1 and are summarised in Table 1.

High temperature rates for the reactions of interest are presented in Table 2. Experimental results by Snooks \textit{et al.}\textsuperscript{15,16} exhibit Arrhenius behaviour for \(Mu + CH_4\) and \(Mu + C_2H_6\), which is indicative that tunnelling effects are insignificant at these temperatures. This is also clear from the fact that the TST results are in good agreement (\textit{i.e.} the error is less than about a factor of 2) with the experimental rates for both \(X + CH_4\) and \(X + C_3H_8\) sets of reactions.

The rates for the \(H + CH_4\) and \(Mu + CH_4\) reactions have been calculated many times with various methods and there are no major differences in our results compared to previous work involving TST, VTST, CVT/\(\mu\)OMT, RPMD and reduced-dimensionality quantum scattering.\textsuperscript{1,2,6,95,96} In fact, these small differences between our results and those reported previously typically fall within the errors of the various PESs used. For instance, the barrier height of the older CBE PES\textsuperscript{50} is approximately 1.4 kJ mol\(^{-1}\) higher than that of the newer PIP-NN PES\textsuperscript{54} we are using in this work, which at 500 K can cause discrepancies of about 40%. We will however, not discuss these subtle differences further, as the comparison between our TST calculations with the MCTDH benchmark on the same PES shows that there are no significant problems associated with the TST approximations which might lead to order-of-magnitude errors.

Less work has been carried out on the \(H + C_2H_6\) reaction as only recently has an accurate potential been fitted.\textsuperscript{97} Canonical variational transition-state theory with the so-called “least-action tunnelling correction” (CVT/LAT)\textsuperscript{98} gives rate constants of 6.0 \(\times\) \(10^{-14}\) cm\(^3\) s\(^{-1}\) and 2.0 \(\times\) \(10^{-13}\) cm\(^3\) s\(^{-1}\) at \(T = 600\) K and 700 K respectively.\textsuperscript{99} These are slightly higher than our TST predictions, which can be partly explained by the fact that the barrier height of their fitted PES is 1.4 kJ mol\(^{-1}\) lower than our \textit{ab initio} value. That there is only a small remaining discrepancy implies that there are no significant corrections introduced by the CVT/LAT approach in this case, implying that the simple TST is adequate for our requirements. In particular, our predicted KIEs are in excellent agreement with experiment.

Therefore, for both \(X + CH_4\) and \(X + C_3H_8\) sets of reactions, TST predicts a strong inverse KIE, which becomes weaker (\textit{i.e.} closer to 1) at high temperatures and is in good agreement.

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**Fig. 2** Tree representation of the ml-MCTDH wavefunction structure and basis set sizes for (a) \(H + CH_4\) (b) \(Mu + CH_4\). See ref. 86 for an explanation of the notation.
with the experimental data. A similar observation was also
made about the X + H₂ reaction² and was also understood by
considering the zero-point energy corrected barrier height,
which is larger for the case X = Mu than X = H.
Considering the good agreement for X + CH₄ and X + C₂H₆,
one would expect that TST should also be valid for X + C₃H₈ at
this temperature range, and a similar KIE trend is predicted.
However, this is in stark contrast with experimental results,¹⁸
which is larger for the case X = Mu than X = H.

### 2.5 Details of the instanton calculations

Instanton rate theory calculations were performed in the low
temperature regime (in this work, 200 to 300 K), where the
quantum tunnelling effect is expected to have a strong con-
tribution to the rate.

Whereas X + CH₄ results were obtained directly using the
PIP-NN PES,³⁴ we employed the machine-learning method of
Gaussian process regression⁴² to obtain ab initio instanton
rates for X + C₂H₆ and X + C₃H₈. This was done in order to
reduce the computational costs associated with on-the-fly
calculations, which would be extreme in the case of the largest
system, X + C₃H₈. The GPR-aided instanton approach has been
shown to reduce the number of ab initio evaluations required by
an order of magnitude without compromising on the accuracy
of the instanton rate calculation.³² In this work, an equivalent
protocol was employed as in ref. 32. To briefly summarise, this
involved the generation of a GPR-based PES from an initial
training set (i.e. consisting of ab initio potentials and
gradients, with points based on an initial guess configuration
of the instanton) which is continuously refined through the
addition of more ab initio potentials, gradients and Hessians
until one obtains a converged instanton rate. This process is
carried out for each reaction and each temperature.

The instanton is expected to be more delocalised at low
temperatures, and also slightly more so in the X = Mu case due
to the lower mass. Due to this, it was thus necessary to include
more ab initio evaluations into the GPR training set at low
temperatures,³⁲ and slightly more so for X = Mu compared to X = H
reactions. However, in all cases, we observed fast convergence,
such that the largest dataset used comprised of 80 poten-
tials, gradients and 13 Hessians, which is a huge computational
saving when compared with an on-the-fly implementation.

We note here that alternative machine-learning approaches
have been employed in instanton calculations based on neural
networks.⁴³,¹⁰² However, we find the GPR approach simpler,
especially seeing as we have a rather small dataset.

In our case, the availability of the GPR-based PES allows us
to employ a large number of beads without excessive computa-
tional overhead. This allows us to eliminate the ring-polymer
discretisation error such that all instanton rates are converged
with respect to N to two significant figures. For all Mu + Y
reactions studied in this work, the number of beads required
for the discretisation was N = 256 at T ≥ 250 K and N = 512 at
T = 200 K in order to obtain converged rates. For the H + Y
reactions, N = 128 beads were enough to achieve converged
rates for the entire low-temperature regime. More beads are
required for the reactions involving Mu because the fluctuation
terms in the instanton rate equation converge slower due to the
increased vibrational frequencies.²¹ Nonetheless, we had no
particular difficulties with running calculations with these
large values of N, but note that for even larger calculations,
alternative methods exist for reducing the computational cost of this procedure. \(^{103}\)

### 3 Results for the low-temperature regime

A representation of the instanton optimised for the \(\text{Mu} + \text{CH}_4\) reaction is shown in Fig. 3. Comparing this to the \(\text{H} + \text{CH}_4\) reaction, which was depicted in ref. 31, one can conclude that the mechanisms are similar despite the replacement of the incoming atom with muonium. It is worth noting here that it is the abstracted H atom which does most of the tunnelling, as is clear from the fact that it is the most delocalised, with relatively small contributions from the incoming Mu and the neighbouring hydrogens. This was expected from the fact that the crossover temperature was almost unchanged by the isotopic substitution, but could only be confirmed by performing an instanton optimisation to find the optimal tunnelling pathway.

Low-temperature rate constants for \(\text{X} + \text{CH}_4\) evaluated with various quantum dynamics approaches are presented in Table 3. Instanton theory, MCTDH and reduced-dimensionality quantum scattering (RD-QS) are all seen to lie with about a factor of 2 of the experimental result at 300 K.

The results of our instanton calculations for \(\text{H} + \text{CH}_4\) using the PIP-NN surface presented here are slightly larger than those predicted using an \textit{ab initio} PES in previous work.\(^{31,32}\) This is simply because the barrier height used here is lower by about 2 \(\text{kJ \text{ mol}^{-1}}\). Likewise, instanton calculations\(^{5} on the CBE PESs\(^{50}\) are about a factor of 2 smaller than those we report here. However, these minor differences are not expected to significantly affect the KIE calculation, for which the barrier height does not directly contribute.

Instanton rates are in good agreement (better than a factor of 2) with MCTDH for both \(\text{H} + \text{CH}_4\) and \(\text{Mu} + \text{CH}_4\), and because these are computed using the same PES, this is a direct test of the approximations inherent in instanton theory. Our instanton results are also of a similar quality as those from RPMD\(^{9}\) calculated on the CBE PES.\(^{50}\) These two comparisons suggest that there are no obvious problems from neglecting anharmonicity and recrossing in the instanton calculation. There is a small discrepancy between RD-QS results, which were obtained using curvilinear coordinates,\(^{56,104}\) and MCTDH for the \(\text{Mu} + \text{CH}_4\) reaction, where the RD-QS rate is too low by an order of magnitude. This may be a consequence of the differences in the PESs used as well as small errors due to the reduced-dimensionality approximation and is thus difficult to disentangle further.

The similar tunnelling factors (defined by the instanton approach) for the \(\text{H}\) and \(\text{Mu}\) variant of the reaction confirms that the tunnelling effect is not strongly influenced by the isotopic substitution. It had been suggested that anharmonicity effects, which are neglected in instanton theory, may play a larger role in \(\text{Mu} + \text{Y}\) reactions.\(^{1,2,105}\) However, the MCTDH results provide a benchmark to test the instanton approximation and the good agreement of the rates shows that the instanton approximation does not in fact introduce significant errors. In fact, the results of the muonium reactions are not seen to be significantly less accurate than those with the incoming H atom. The KIE prediction is expected to be especially accurate as some cancellation of errors is expected to occur,\(^{8}\) which at least partly explains why the neglect anharmonicity is not a major problem. Instanton theory predicts a KIE at 300 K of 1.6 \(\times 10^{-4}\), which is in good agreement with the prediction from MCTDH of 2.0 \(\times 10^{-4}\).

We had already reported \textit{ab initio} instanton results for \(\text{H} + \text{C}_2\text{H}_6\) (but not \(\text{Mu} + \text{C}_2\text{H}_6\)) in ref. 32. These results were seen to be in good agreement with experiment as well as various other quantum rate theories such as semiclassical transition-state theory\(^{106}\) and RD-QS.\(^{56}\) Table 4 reproduces some of these results alongside newly calculated rate constants for \(\text{Mu} + \text{C}_2\text{H}_6\). Recently CVT/LAT\(^{99}\) calculations on the newly constructed PES by Espinosa-Garcia et al.,\(^{97}\) gave rates of 4.60 \(\times 10^{-11}\) cm\(^3\) s\(^{-1}\) and 2.09 \(\times 10^{-10}\) cm\(^3\) s\(^{-1}\) at \(T = 300\) K and 200 K respectively and are thus within the same order of magnitude as our instanton results. This good agreement implies that the simpler one-dimensional tunnelling correction provides a good approximation to the full-dimensional instanton analysis in this case.

Fig. 4 shows the instanton pathway for \(\text{Mu} + \text{C}_2\text{H}_6\). Here, similar behaviour to \(\text{X} + \text{CH}_4\) and \(\text{H} + \text{C}_2\text{H}_6\) (see ref. 32) can be observed, with the abstracted H atom again doing most of the
that as expected the X + i-C₃H₈ channel gives the dominant contribution to the rate constant and the other two channels can effectively be neglected without affecting our rate prediction at this temperature by more than 5%. A similar conclusion was reached in ref. 104. To test this assertion at lower temperatures, we calculated instantons for X + n₁-C₃H₈ and found that the ratio between X + i-C₃H₈ and X + n₁-C₃H₈ increases even further. The instantons representing reactions in these two channels are shown in Fig. 5.

Table 6 presents the calculated instanton rates for X + C₃H₈ at (T ≤ 300 K) alongside experimental and other theoretical values if available for comparison. In particular, it can be observed that the instanton rate calculations for the H variant of the reaction are in good agreement with the experimental measurement at 300 K by Tsang et al.¹⁰¹ The instanton results differ from those of the RD-QS calculations by a factor of two at 300 K (increasing to a factor of four at 200 K). This relatively minor discrepancy is due to a number of differences between the approaches. On one hand instanton theory employs a semiclassical approximation to the full-dimensional problem, and on the other exact quantum scattering theory is applied to a reduced-dimensionality approximation of the system. In addition, slightly different electronic-structure methods were used in the calculations. The RD-QS builds a two-dimensional surface of CCSD(T)-F12 energies corrected by harmonic zero-point energies evaluated by MP2. The barrier height we obtain with a full UCCSD(T)-F12b/cc-pVDZ-F12 calculation is approximately 2 kJ mol⁻¹ higher than that with the dual-level approach based on geometries optimised with MP2, which may explain why the RD-QS rates are about a factor of two larger than the instanton predictions at 300 K. It is expected that the almost perfect agreement between RD-QS and experiment at 300 K is partly due to a fortuitous cancellation of errors, and one should simply conclude that both instanton theory and RD-QS are reliable at predicting the correct order of magnitude of the rate at this temperature.

For the Mu + C₃H₈ reaction, no other theoretical predictions are available in the literature. However an experimental value has been measured at 300 K.¹⁰² The observed rate at 300 K is more than three orders of magnitude larger than our instanton prediction.

Very recently more experimental rates were reported in the range 300–435 K.¹⁰³ Most of these new rates are close to or larger than the cross-over temperature (see Table 1), where semiclassical theory predicts that the deep-tunnelling mechanism via the instanton tunnelling pathway no longer exists and that a shallow-tunnelling mechanism becomes dominant. For this, simpler tunnelling-correction approaches are expected to become valid. We thus apply the Eckart tunnelling correction at

| Y       | Degeneracy | H + Y    | Mu + Y   |
|---------|------------|----------|----------|
| i-C₃H₈  | 2          | 2.9 (−16) | 8.3 (−20) |
| n₁-C₃H₈ | 2          | 2.3 (−18) | 7.5 (−22) |
| n₂-C₃H₈ | 4          | 4.0 (−18) | 1.1 (−21) |

Fig. 4 As Fig. 3 for Mu + C₃H₈.

Table 5 Calculated instant rate constants, $k^{\text{H}+Y}$ and $k^{\text{Mu}+Y}$ (where Y specifies the channel involved), at 300 K for individual channels of the X + C₃H₈ reaction. All rates are in cm³ s⁻¹. The total rates presented in Table 6 are found by summing over these individual rates multiplied by the degeneracy of the channel.
The unexpected KIE has been attributed to tunnelling effects in the Mu + C₃H₈ reactions.¹⁷,¹⁸ Our instanton calculations however refute this and predict that tunnelling plays a similar role in the H + C₃H₈ reactions.¹⁷,¹⁸ The good agreement between the predictions for H + C₃H₈ and experimental results confirms that the ab initio PES is accurate and that the GPR fitting procedure is also applicable to this system, which is larger than those we have applied it to previously. The trends also confirm that the shallow-tunnelling correction gives an accurate description at temperatures above 300 K.

Based on our findings for H + C₃H₈ one would expect that the same approach would also be valid for Mu + C₃H₈. However, not only are the values of the rates different, our prediction for the slope of the Arrhenius plot is much steeper than the experimental observations, as shown in the bottom plot of Fig. 6. Even more surprising is that the trend in the experimental KIEs is opposite to that which we have calculated, i.e. the values of the experimental KIE increase with decreasing temperature whereas ours decrease. This results in a experimental KIE at 300 K which is reported¹⁷,¹⁸ to be more than three orders of magnitude larger than what our calculations predict.

The tunnelling factors κ_{tun} are thus given by

\[
\kappa_{\text{tun}} = \begin{cases} 
\frac{\beta \epsilon_{\text{tun}}}{\kappa_{\text{inst}}/\kappa_{\text{TST}}} & T > 300 \text{ K} \\
0 & T \leq 300 \text{ K}
\end{cases}
\]

where \(\epsilon_{\text{tun}}\) is the barrier height and \(\tau(E)\) is the transmission probability for an asymmetric Eckart barrier parameterized to reproduce the barrier height, imaginary frequency and exothermicity. In Fig. 6 and Table 6, we compare the results from this work as well as experimental data for H + C₃H₈ and Mu + C₃H₈. TST calculations with Eckart tunnelling corrections are shown by the red line in Fig. 6 at data points where \(T > 300 \text{ K}\), whereas data points for \(T \leq 300 \text{ K}\) correspond to instanton calculations. Here it can be observed that the addition of tunnelling corrections shifts the TST results closer to the experimental data for H + C₃H₈, implying that the tunnelling correction gives a good description of the reaction. There is a small kink in the predicted line as the instanton calculation does not match perfectly with the Eckart-corrected TST results. However, this minor discrepancy is on the order of less than a factor of 2.

The unexpected KIE has been attributed to tunnelling effects in the Mu + C₃H₈ reactions.¹⁷,¹⁸ Our instanton calculations however refute this and predict that tunnelling plays a similar role in the H + C₃H₈ reactions.

\[\begin{array}{ccc}
T (K) & H + C₃H₈ & \text{This work} \\
700 & 1.5 & 4.2 (-13) \\
600 & 1.7 & 4.1 (-13) \\
500 & 2.1 & 3.4 (-14) \\
435 & 2.7 & 1.1 (-14) \\
397 & 3.4 & 5.0 (-15) \\
358 & 4.7 & 2.0 (-15) \\
324 & 6.9 & 8.1 (-16) \\
300 & 14 & 5.9 (-16) \\
250 & 27 & 6.6 (-17) \\
200 & 180 & 6.8 (-18) \\
\end{array}\]

\[\begin{array}{ccc}
T (K) & Mu + C₃H₈ & \text{This work} \\
700 & 1.5 & 4.0 (-14) \\
600 & 1.7 & 7.3 (-15) \\
500 & 2.2 & 7.7 (-16) \\
435 & 2.8 & 1.1 (-16) \\
397 & 3.5 & 2.8 (-17) \\
358 & 4.8 & 5.4 (-18) \\
324 & 7.1 & 9.9 (-19) \\
300 & 14 & 3.3 (-19) \\
250 & 35 & 7.4 (-21) \\
200 & 1220 & 2.2 (-22) \\
\end{array}\]

Tunneled factors and KIEs for X + C₃H₈ in this work, evaluated with instanton theory (\(T \leq 300 \text{ K}\)) and TST with Eckart tunnelling corrections (\(T > 300 \text{ K}\)). Experimental and RD-QS results are also presented for comparison, where available.

Tables

| H + C₃H₈ | This work | RD-QS⁵⁶ | Expt.¹⁰¹ |
|---------|-----------|---------|----------|
| 700     | 1.5       | 4.2 (-13) | 6.1 (-13) | 8.7 (-13) |
| 600     | 1.7       | 1.4 (-13) | 2.3 (-13) | 3.2 (-13) |
| 500     | 2.1       | 3.4 (-14) | 6.5 (-14) | 8.9 (-14) |
| 435     | 2.7       | 1.1 (-14) | —         | 3.1 (-14) |
| 397     | 3.4       | 5.0 (-15) | 1.2 (-14)⁵ | 1.5 (-14) |
| 358     | 4.7       | 2.0 (-15) | 4.2 (-15)⁶ | 5.9 (-15) |
| 324     | 6.9       | 8.1 (-16) | —         | 2.3 (-15) |
| 300     | 14        | 5.9 (-16) | 1.1 (-15) | 1.1 (-15) |
| 250     | 27        | 6.6 (-17) | 2.3 (-16) | —         |
| 200     | 180       | 6.8 (-18) | 3.3 (-17) | —         |

| Mu + C₃H₈ | This work | Expt.¹⁸ |
|-----------|-----------|---------|
| 700       | 1.5       | 4.0 (-14) |
| 600       | 1.7       | 7.3 (-15) |
| 500       | 2.2       | 8.7 (-16) |
| 435       | 2.8       | 2.8 (-17) |
| 397       | 3.5       | 5.4 (-18) |
| 358       | 4.8       | 9.9 (-19) |
| 324       | 7.1       | 3.3 (-20) |
| 300       | 14        | 7.4 (-21) |
| 250       | 35        | 9.4 (-22) |
| 200       | 1220      | 2.2 (-22) |

KIE

| This work | Expt. |
|-----------|-------|
| 700       | 0.10  |
| 600       | 0.11  |
| 500       | 0.19  |
| 435       | 0.0057|
| 397       | 0.11  |
| 358       | 0.19  |
| 324       | 0.0012|
| 300       | 0.41  |
| 250       | 0.56  |
| 200       | 0.81  |

RD-QS values at 397 and 358 K are approximated by results reported at 400 K and 350 K respectively.

Fig. 6 Rates for H + C₃H₈ (top) and Mu + C₃H₈ (bottom) calculated using TST, Eckart-tunnelling corrected TST (\(T > 300 \text{ K}\)) and instanton theory (\(T \leq 300 \text{ K}\)). These are compared with the experimental rates from ref. 18 and 101.
role as for the other two classes of reactions studied in this paper. Although the tunnelling factor at 200 K is larger for Mu + C_3H_8 than for H + C_3H_8, at 300 K and above the tunnelling factors are approximately the same.

As demonstrated previously, for the hydrogen abstraction reactions, the atom most involved in the tunnelling process is the abstracted H atom, and tunnelling is only weakly dependent on the mass of the incoming reactant atom. We can quantify this by computing the contributions of various atoms to the squared mass-weighted path length of the instanton (called \( R_n \) in ref. 21), which is proportional to the ring-polymer spring energy. The contribution from the incoming atom (regardless of whether it is H or Mu) was found to be no more than 12% for all reactions studied. In contrast, the abstracted H atom contributes at least 70% of the squared mass-weighted path length, and thus dominates the tunnelling process. Overall we observed only a 15–45% increase in the squared mass-weighted path length for reactions with Mu compared to those with H. In contrast, it increases more than five-fold when the temperature is decreased from \( T = 300 \) K to \( T = 200 \) K. This explains why temperature is a much more important factor in our predicted KIEs than the mass of the incoming atom.

In order to explain the discrepancy between the experimental and theoretical results for Mu + C_3H_8, it will be necessary to find the source of error. If the instanton prediction at 300 K is incorrect, it must be shown why this error lowers the Mu + C_3H_8 reaction by three orders of magnitude, but not the other reactions considered here, which are in good agreement with experiment.

There are a number of approximations involved in the ab initio instanton approach which are potential sources of error in the predicted rate. As already stated, we can eliminate the discretisation error by using a large number of ring-polymer beads. However even in this limit, instanton theory neglects recrossing effects and uses semiclassical approximations which are equivalent to treating the fluctuations around the dominant tunnelling pathway harmonically. Due to the light mass of Mu, one might expect that the reaction path is strongly skewed leading to more recrossing. However, the neglect of recrossing typically overpredicts rates and thus this cannot explain why our predicted rate is too low. As mentioned in various studies,\(^{1,2,104,109}\) an accurate treatment of vibrational modes is necessary for these reactions, with the large vibrational frequencies introduced by the abstraction process through the formation of clusters. The possibility of roaming dynamics\(^{10,111}\) influencing the rate constant was also considered and briefly investigated. We explored possible configurations in an attempt to find a minimum describing a bound \( \text{X} + \text{C}_3\text{H}_8 \) complex, from which a unimolecular dissociation into \( \text{XH} + \text{C}_3\text{H}_7 \) might occur. However, despite many attempts, we were not able to find such a configuration. In order to go beyond instanton theory to treat recrossing and anharmonicity more accurately and also allow for the possibility of roaming trajectories, a ring-polymer molecular dynamics simulation could be carried out.\(^{112,113}\) However, this would require the construction of a globally-accurate PES, which is not currently available.

The quality of the PES directly ties in to the accuracy of the rates calculated by various quantum dynamics approaches, including instanton theory. This has in fact been observed in the calculation of the H + CH_4 rates at high temperatures using various quantum dynamics approaches, wherein the accuracy of the PES matters more than the quantum dynamics approach.\(^{1,2,8,109}\) In this work, we used coupled-cluster theory with F12 methodology, which is expected to give energies near the basis-set limit.\(^{19}\) This has been demonstrated in various work for similar systems,\(^{12,114}\) including the calculation by Horsten et al. \(^{56}\) That our high-temperature TST results match well with experiment suggests that at least the barrier heights and frequencies are accurately described by this method.

From the H + C_3H_8 results, we can infer that the PES is accurate as it should be identical to that of H + C_3H_8, within the Born–Oppenheimer approximation. Truhlar has suggested that due to the small mass of Mu, the validity of the Born–Oppenheimer approximation should be questioned.\(^{2}\) However, he does not suggest that it would be a major source of error and that it would perhaps change rates by a factor of two at most.

In this work, a local representation of the PES was generated with GPR. We find that this approach gives smooth surfaces which converge as the training set is increased. In previous work, we showed that this GPR-aided approach gives exactly the same rate for an on-the-fly instanton calculation for H + CH_4.\(^{32}\) Considering that the approach has also been shown to be successful for H + C_2H_6 and now for H + C_3H_8 as well, we see little reason as to why it should not work for Mu + C_3H_8.

4 Conclusions

We have evaluated rate constants for Mu + CH_4, Mu + C_2H_6, and Mu + C_3H_8 and their equivalent reactions with H. In the case of X + C_2H_6 and X + C_3H_8, we have employed GPR to reduce computational costs while retaining an accuracy similar to that of an ab initio instanton rate calculation. Our instanton calculations show that although tunnelling has a significant effect on the rate at 300 K for these reactions, it speeds up the Mu + Y reactions by the same factor as H + Y and it can therefore be ruled out as the major contributor to the KIE at 300 K and above.
Our results for the H + X reactions agree well with experimental measurements and other theoretical predictions, which suggests that the potential-energy surfaces are of sufficient accuracy. Additionally, we have performed MCTDH calculations for Mu + CH₄ on the same PES as a benchmark to ascertain how the approximations made by instanton rate theory affect the rate constant. For the Mu + CH₄ reaction, we observe good agreement between the instanton rate theory results and MCTDH calculations, which suggest that the approximations made by instanton rate theory (such as the neglect of anharmonicity perpendicular to the path and recrossing) are not detrimental to the study of this reaction.

We argue that our instanton rate calculations are accurate for the Mu + C₂H₆ and Mu + C₃H₈ reactions as well, as the predicted mechanisms are similar to that of Mu + CH₄. However, our Mu + C₃H₈ prediction did not reproduce the unexpected experimental result by Fleming et al.¹⁷,¹⁸ whereas no experimental or benchmark results were available for comparison for Mu + C₂H₆ at low temperatures. The cause of the discrepancy thus remains unidentified and further studies need to be conducted in order to understand and explain it.

We do however provide evidence to argue that the experimental KIE is not caused by tunnelling effects. It is also unlikely that including recrossing effects would provide the explanation as this could only reduce the predicted rate further away from the experimental result. If an accurate full-dimensional fitted PES were available, one could use RPMD to check whether significant anharmonic effects are present which can explain the result. A simpler alternative may be the VPT2 approach of Clary and coworkers¹¹,¹⁰⁶,¹¹⁵ which treats tunnelling less accurately than instanton theory, but has a perturbative approach to anharmonicity in all modes, which may shed light on whether the anharmonic effects are important.

It would also be useful to confirm whether the Mu + C₃H₈ reaction is fundamentally different from Mu + CH₄ and Mu + C₂H₆. Currently experiments have not been reported which measure the rates of both reactions within the same temperature range. Therefore, if new experimental results for Mu + CH₄ and Mu + C₂H₆ at 300 K (even if they were simply to find an upper bound to the rate) or Mu + C₃H₈ at high temperatures were available, this would allow better benchmarking of the theoretical predictions and potentially help hunt down the source of the discrepancy.

Theoretical studies of H + n-C₆H₁₄ have shown that tunnelling effects enhance the rate by 1–2 orders of magnitude at 300 K.¹¹⁶ Although we have not tackled the X + n-C₆H₁₄ reaction in this work, we expect that when studied with instanton theory it will behave similarly to the other reactions, and that tunnelling effects of H + n-C₃H₈ will be similar to those of Mu + n-C₃H₈ such that making hard to explain the unexpected KIEs observed in ref. 18.

On a positive note, this study provides further evidence that the GPR-aided instanton approach¹² can be employed efficiently to study polyatomic reactions. The calculations do not require reduced-dimensionality approximations or compromise on the electronic-structure method. We thus expect the approach to be widely applicable to a variety of large and complex systems.

For instance, while abstraction reactions result in an inverse KIE (i.e. the H variant of the reactions have a larger rate compared to the Mu variant), it is known that for addition reactions involving Mu (e.g. Mu + C₂H₄,¹¹⁷ Mu + C₂H₂,¹¹⁸ and Mu + C₄H₁₀) tunnelling makes much larger contributions. Other similar reactions of interest include Mu + F₂ (for which a large KIE is observed)¹²⁰ and reactions with muonic helium (Heₐ = [³He⁺ e⁻]), such as Heₐ + CH₄.¹⁰⁵ The GPR-aided instanton approach would be an excellent candidate for the study of these reactions too.

Conflicts of interest
There are no conflicts to declare.

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