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# Can quasiclassical trajectory calculations reproduce the extreme kinetic isotope effect observed in the muonic isotopologues of the $H + H_2$ reaction?

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Rate coefficients for the mass extreme isotopologues of the  $H + H_2$  reaction, namely,  $Mu + H_2$ , where  $Mu$  is muonium, and  $He\mu + H_2$ , where  $He\mu$  is a He atom in which one of the electrons has been replaced by a negative muon, have been calculated in the 200–1000 K temperature range by means of accurate quantum mechanical (QM) and quasiclassical trajectory (QCT) calculations and compared with the experimental and theoretical results recently reported by Fleming *et al.* [Science **331**, 448 (2011)]. The QCT calculations can reproduce the experimental and QM rate coefficients and kinetic isotope effect (KIE),  $k_{Mu}(T)/k_{He\mu}(T)$ , if the Gaussian binning procedure (QCT–GB) – weighting the trajectories according to their proximity to the right quantal vibrational action – is applied. The analysis of the results shows that the large zero point energy of the  $MuH$  product is the key factor for the large KIE observed. © 2011 American Institute of Physics. [doi:10.1063/1.3611400]

## I. INTRODUCTION

Kinetic isotope effects (KIEs) have traditionally provided valuable information about chemical mechanisms. In reactions with a barrier, a primary effect of isotopic substitution, already recognized in the early literature on chemical kinetics, is the modification of the zero point energy (ZPE) of reactants, products, and transition state, which can result in an appreciable variation of the activation energy (see, for instance, Refs. 1–4 and references therein). Other effects of isotopic substitution such as those related to tunneling, internal excitation, changes in the minimum energy path, and location of the transition state, or preferential energy transfer to a given bond have been considered in later publications.<sup>5–9</sup> For obvious reasons, the largest KIEs observed correspond to hydrogen isotopes.

In a recent article, Fleming *et al.*<sup>10</sup> have reported a joint experimental and theoretical investigation of the KIE in the paradigmatic  $H + H_2$  reactive system for an extremely large mass ratio. The study constitutes a test of basic concepts in chemical kinetics.<sup>11</sup> Two special isotopic variants of the reaction based on muonic atoms, namely,  $Mu + H_2$  and  $He\mu + H_2$ , were considered by the authors. The first reaction, whose rate coefficient,  $k(T)$ , had been previously

determined,<sup>12</sup> involves  $Mu$ , a light atom of 0.114 u formed by a positive muon,  $\mu^+$ , and an electron. For the second reaction, the authors used muonic helium,  $He\mu$ , with a mass of 4.116 u in which one of the He electrons is replaced by a negative muon,  $\mu^-$ . From a chemical point of view,  $He\mu$  can be considered as an isotope of H since  $\mu^-$ , 207 times heavier than an electron, occupies an orbital very close to the nucleus and screens effectively the charge of one proton. With a mass ratio of 36.1 between their atomic reactants, the two reactions represent an extreme case of isotopic variation.

The authors of the mentioned work<sup>10</sup> compared the rate coefficient measurements, performed with muon beams in the TRIUMF accelerator, to rigorous quantum mechanical (QM) calculations of the reaction dynamics based on the outgoing wave variational principle,<sup>13</sup> and with approximate variational transition state theory (VTST) calculations<sup>14</sup> without and with multidimensional tunneling contributions<sup>15</sup> to help in the mechanistic interpretation. An accurate *ab initio* potential energy surface, PES, incorporating the diagonal correction to the Born–Oppenheimer PES (adiabatic approximation)<sup>16</sup> was used in the dynamical studies. The QM rate coefficients were in very good agreement with the measurements for  $He\mu + H_2$  at 405 and 500 K, but the value at 295 K was smaller than the measured point by 30%. A somewhat worse, but still quite acceptable accordance (within 25% of the QM result) was found with the VTST calculations incorporating tunneling corrections, whereas appreciable lower rate coefficients were obtained when tunneling corrections were not included. The two sets of measurements with muonic atoms<sup>10,12</sup>

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presented an overlap at 500 K, where the KIE, estimated as the ratio between the rate coefficients for the  $\text{Mu} + \text{H}_2$  and  $\text{He}\mu + \text{H}_2$  reactions, ( $k_{\text{Mu}}/k_{\text{He}\mu}$ ), was found to be 0.0108, very well accounted for by the QM calculations (0.0104). From the analysis of their results, the authors concluded that this marked isotope effect may be attributed primarily to the difference in the stretching-vibration ZPE at the two transition states.

Ever since the advent of transition state theory, the properties of the quantum states of transition states in direct reactions and their possible manifestation on dynamical observables, has attracted great attention. However, the observation of effects distinctly attributable to these quantized states is proving extremely difficult.<sup>17,18</sup> In the 1990s, Truhlar *et al.* applied to bimolecular reactions the concept of dynamical bottlenecks<sup>19–21</sup> based on the quantized levels of the transition state that would act as effective barriers to reaction. These authors noted that the bottlenecks could be identified in the undulations appearing in the derivative of the QM cumulative reaction probabilities (CRPs) with respect to the energy, but undulations have also been found in the derivatives of the CRP calculated using quasiclassical trajectories (QCTs).<sup>22,23</sup> Recent experimental results showing oscillations in the energy evolution state-to-state differential cross sections (DCS) for the  $\text{D} + \text{H}_2$  reaction were interpreted as interferences from different bottleneck states,<sup>24</sup> but again similar (though not identical) oscillations have been found in QCT calculations.<sup>25,26</sup> Furthermore, analogous oscillations measured recently in the DCS of the  $\text{F} + \text{HD}$  reaction were attributed to reactive resonances<sup>27,28</sup> rather than to the opening of thresholds associated with dynamical bottlenecks. Finally, a shift in the threshold with reactants' helicity, reported for the  $\text{D} + \text{H}_2$  reaction and attributed to the concurrence of different bottleneck states,<sup>29,30</sup> has also found a classical counterpart that provides an explanation in terms of stereodynamical constraints.<sup>23</sup>

The previous examples illustrate the difficulty in the unequivocal assignment of specific experimental results to the exclusive influence of quantization of the transition state in direct reactions. Other effects might also be at play and, in this respect, the comparison between classical and QM treatments of the reaction dynamics can be enlightening. In this study, we present such a comparison for the rate coefficients and KIE observed in the reactions of muonic atoms with  $\text{H}_2$ . To this end, accurate QM as well as QCT calculations have been carried out in order to determine the rate coefficients for the  $\text{Mu} + \text{H}_2$  and  $\text{He}\mu + \text{H}_2$  reactions over the 200–1000 K temperature range.

The paper is structured as follows. In Sec. II, we will briefly describe the methods used in the calculations. The results and discussion will be presented in Sec. III followed by a summary and the main conclusions of this work in Sec. IV.

## II. THEORETICAL METHODOLOGY

QM and QCT calculations were performed on the BKMP2 PES of Boothroyd *et al.*<sup>31</sup> covering the range of collision energies and initial quantum states necessary to determine rate coefficients for the  $\text{Mu} + \text{H}_2$  and  $\text{He}\mu + \text{H}_2$

reactions over the 200–1000 K temperature interval. A description of the theoretical methods has been presented elsewhere<sup>22,32</sup> and only the details relevant for the present work will be given here.

The QCT  $k(T)$  for the two isotopologues were determined in the whole range of temperatures following the CRP formalism described in Refs. 22 and 23. Although the total CRP and the thermal CRP as a function of the total energy were also obtained,<sup>22</sup> the rate coefficients can be calculated directly with the sampling employed without needing to determine the total CRP and avoiding the numerical integration (see Ref. 22). To this purpose, batches of  $10^7$  trajectories in the 0.5–1.6 eV energy range were run. In addition, to further check the accuracy and reproducibility of the rate coefficients, especially at low  $T$ , a series of batches of trajectories were run at specific temperatures using the standard (but less efficient) method based on the sampling of the collision and internal energies from the corresponding Maxwell–Boltzmann distributions and a continuous sampling of impact parameters. The results of the two methods were identical within their statistical uncertainties.

For the classical quantization of the products' states, two procedures have been used. The first of these methods, the standard histogrammatic binning (QCT–HB), consists in rounding the classical (real value) vibrational quantum numbers to their nearest integers, which effectively implies that all reactive trajectories have the same weight irrespective of their final vibrational action. However, this rounding procedure may allow the population of states that are energetically closed; in particular, with classical internal energies below that of the ground state of the products. To overcome this problem, as in previous works, we have used the Gaussian binning (QCT–GB) method<sup>33,34</sup> whose implementation has been described in Ref. 35. Briefly, it consists in weighting each trajectory according to Gaussian functions centered on the right QM vibrational action, in such a way that the closer the vibrational (real value) quantum number of a given trajectory to the nearest integer, the larger will be the weighting coefficient for that trajectory. This method has been successfully applied in many works during the last years (see, for instance, Refs. 36–39). In the present study as in previous works, we have used a full-width-half-maximum of  $\Delta\nu=0.1$  for the Gaussian functions. The results for the  $\text{He}\mu + \text{H}_2$  reaction are largely insensitive to this value but, as will be discussed hereinafter, the  $k_{\text{Mu}}(T)$  values are considerably affected by changes in this parameter. In practice, trajectories whose vibrational action is sufficiently far from the quantal one contribute very little to the total cross section. As a consequence, the ZPE requirement is effectively enforced at the expense of a possible decrease of the reactivity.

Extensive fully converged time independent QM calculations were carried out using the coupled-channel hyperspherical coordinate method.<sup>32</sup> For  $\text{Mu} + \text{H}_2$ , results were obtained for a grid of 280 total energies in the range of 0.5 eV to 2.0 eV. All partial waves up to  $J_{\text{max}} = 25$  and helicity quantum numbers up to  $k = J_{\text{max}}$  were included. The maximum hyper-radius was set at  $25 a_0$  and 250 log-derivative sectors were propagated. All the diatomic levels up to  $E_{\text{max}}=2.85$  eV had to be included in the basis. For  $\text{He}\mu + \text{H}_2$ , a  $J_{\text{max}} = 41$  and

$k_{\max} = 6$  ensured convergence. In this case, calculations span total energies in the 0.4–1.6 eV interval. The diagonal correction was introduced in the QCT and QM calculations as in Ref. 40 by applying the Boltzmann factor  $\exp[-\Delta E_b/k_B T]$ , where  $\Delta E_b$  is the increase in the barrier height<sup>10</sup> (16.04 meV and 5.51 meV for MuH<sub>2</sub> and He $\mu$ H<sub>2</sub>, respectively), to the  $k(T)$  calculated on the BKMP2 PES. For the purposes of this work, the differences with respect to the rate coefficients determined on the recent, highly accurate PES that incorporates the diagonal correction<sup>16</sup> are irrelevant.

### III. RESULTS AND DISCUSSION

The Arrhenius plot of the QM and QCT rate coefficients for the Mu + H<sub>2</sub> reaction together with the experimental measurements of Reid *et al.*<sup>12</sup> is shown in Fig. 1. The QM calculations lead to the best agreement with experiment and produce  $k_{\text{Mu}}(T)$  which are essentially within the experimental uncertainty. The QCT–GB method performs also reasonably well, although deviations with respect to the QM results are observed. In particular, for temperatures higher than 500 K, where experimental data are available, the QCT–GB  $k_{\text{Mu}}(T)$  are smaller than the respective QM values by about 35%. In contrast, the QCT–HB  $k_{\text{Mu}}(T)$  grossly overestimate the QM and experimental results. For this reaction, most reactive trajectories for the relevant collision energies lead to a classical vibrational energy below the large ZPE (0.5930 eV) of the MuH molecule (*vide infra*); it is thus not surprising that the values of the QCT–GB  $k_{\text{Mu}}(T)$  are strongly affected by the width of the Gaussian distribution. At  $T = 500$  K, their values range from  $3.69 \times 10^{-16}$  cm<sup>3</sup> s<sup>-1</sup> for  $\Delta\nu = 0.15$  to  $1.45 \times 10^{-16}$  cm<sup>3</sup> s<sup>-1</sup> for  $\Delta\nu = 0.05$ , respectively, as compared to  $2.16 \times 10^{-16}$  cm<sup>3</sup> s<sup>-1</sup> obtained for  $\Delta\nu = 0.1$ . Although the difference is considerable, these values are well below that obtained with the QCT–HB procedure. The choice of  $\Delta\nu = 0.1$ , which is a value commonly used, is based on the comparison of the thresholds

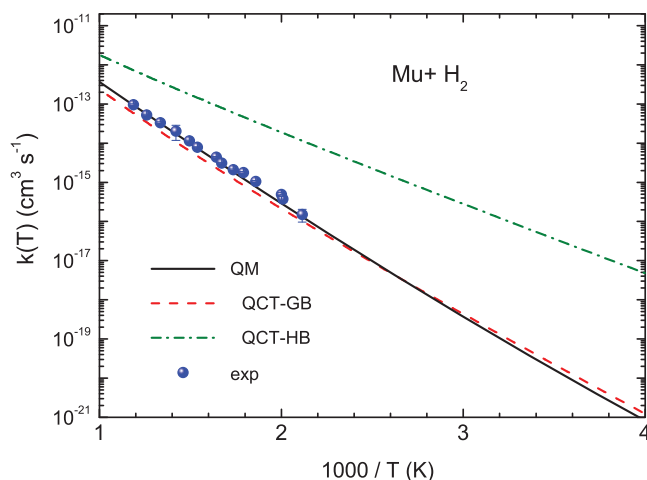


FIG. 1. Arrhenius plot showing the comparison of the experimental rate coefficients (blue solid circles) (Ref. 12) for the Mu + H<sub>2</sub> reaction (Mu  $\equiv$  <sup>0.11</sup>H) with the present QM (black solid line), QCT–GB (red dashed line), and QCT–HB (green dotted–dashed line) calculations of the rate coefficients using the BKMP2 PES with the diagonal correction.

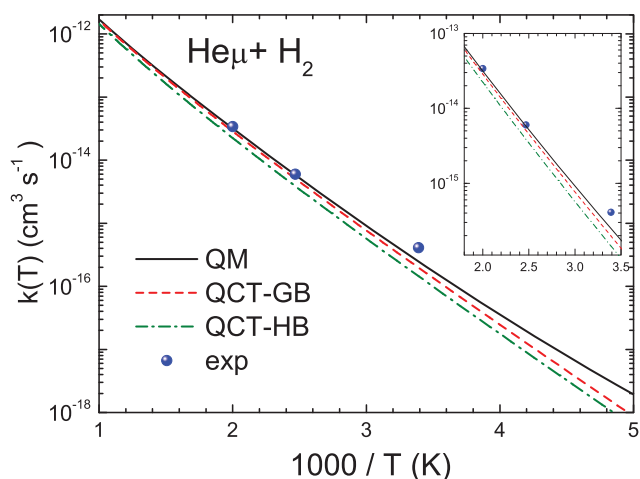


FIG. 2. Same as Fig. 1, but for the He $\mu$  + H<sub>2</sub> reaction (He $\mu$   $\equiv$  <sup>4.11</sup>H). Experimental points (blue solid circles) from Ref. 10. The inset portrays an enlargement of the range of temperatures (285–550 K) covered by the experimental measurements (Ref. 10).

in the thermal CRP, whose integral over the total energy divided by the reactant's partition function renders the rate coefficient at a given  $T$ . In spite of the differences between the shapes of the QCT–GB and QM thermal CRPs, it has been found that for  $\Delta\nu = 0.1$ , the total energy threshold is in very good coincidence with that corresponding to the QM calculation, whereas those for  $\Delta\nu = 0.15$  and  $\Delta\nu = 0.05$  fall well below and above the QM one, respectively. Similar agreement is found in the comparison of the thresholds in the CRP for  $J = 0$ .

The results for the He $\mu$  + H<sub>2</sub> reaction are represented in Fig. 2. The level of agreement between the present QM calculations and the experimental data is the same as that reported for the QM calculations in Ref. 10. The QCT–GB  $k_{\text{He}\mu}(T)$  are also in good accordance with those from QM calculations, although they diverge gradually toward lower values with decreasing temperature, which is suggestive of QM tunneling. Note that for this reaction, the QCT–HB procedure leads also to reasonable results. The QCT–HB  $k(T)$  are lower than those from QM, from QCT–GB and from experiment, but the differences are much smaller than those for Mu + H<sub>2</sub>. In contrast to MuH, the He $\mu$ H molecule has a comparatively low ground vibrational level (0.2136 eV) and the fraction of reactive trajectories leading to vibrational energies below this level is smaller. Indeed, Fig. 3 shows the classical vibrational distributions for the formation of MuH and He $\mu$ H from the reactants at  $T = 500$  K illustrating the effect of the Gaussian binning and the standard HB procedures. As can be seen, the classical vibrational distribution for the MuH product is strongly shifted towards negative values of  $\nu'$ , such that only a small fraction falls within the Gaussian curve. In this case, the cross section is enormously diminished with respect to that resulting from the uniform weighting of the HB method. In contrast, the vibrational distribution for the He $\mu$ H product is much broader and the fraction of the distribution within the Gaussian curve is considerable. The main consequence is that the QCT–GB  $k(T)$  for the He $\mu$  + H<sub>2</sub> reaction are only slightly affected by the width of the Gaussian weight

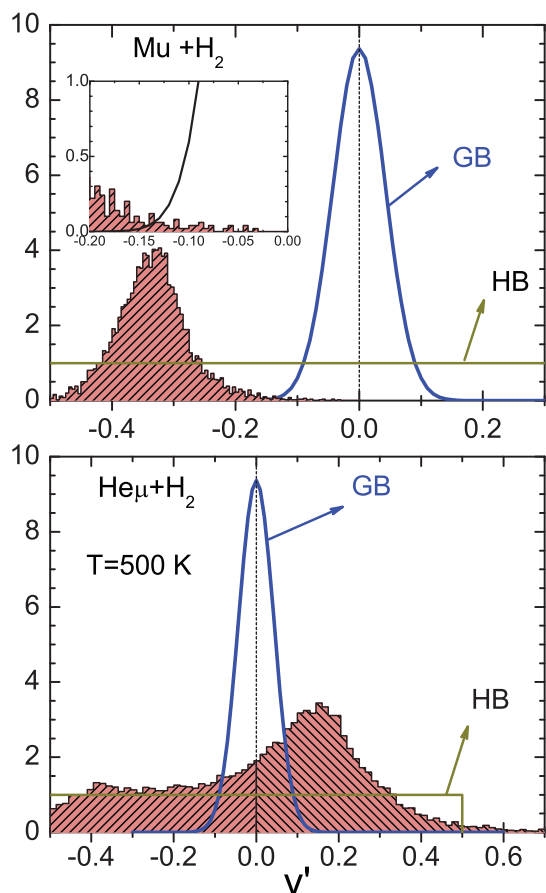


FIG. 3. Classical vibrational distribution for the  $\text{MuH}$  and  $\text{He}\mu\text{H}$  molecules from the  $\text{Mu} + \text{H}_2$  (top) and  $\text{He}\mu + \text{H}_2$  (bottom) reactions at  $T = 500$  K. The weighting functions for the standard histogram and Gaussian binning procedures are also shown and serve to illustrate the differences between the two final state assignments. Note the difference between the vibrational distributions of the two reactions that explain why the GB procedure diminishes the cross section for the  $\text{Mu} + \text{H}_2$ , whereas slightly enhances that for the  $\text{He}\mu + \text{H}_2$  reaction.

used for the binning. In fact, the value derived by weighting the classical vibrational distribution with the Gaussian curve is slightly larger than that obtained with the HB procedure, which is simply the integral of the vibrational distribution over the  $v' \in [-0.5, 0.5]$  interval. Nonetheless, the difference is not very significant.

The evolution of the KIE with temperature is shown in Fig. 4, where the calculated  $k_{\text{Mu}}(T)/k_{\text{He}\mu}(T)$  is compared with the experimental point<sup>10,12</sup> at  $T = 500$  K. The present QM result (0.0091) reproduces only slightly worse the measured value than that from Ref. 10. The KIE calculated with the QCT-GB method is 0.0074, still in reasonable agreement with the measurements, but that from the QCT-HB calculation is two orders of magnitude larger, due to the already mentioned inability of this method to account for the rate coefficient of the reaction with Mu. The QM and QCT-GB  $k(T)$  ratios present a similar evolution with temperature over the range considered. In contrast, the QCT-HB  $k_{\text{Mu}}(T)/k_{\text{He}\mu}(T)$  is a much weaker function of temperature and tends to  $\approx 1.3$  for high  $T$  values.

Fleming *et al.*<sup>10</sup> assumed that the marked KIE observed in the experiment and in the QM calculations is due to the

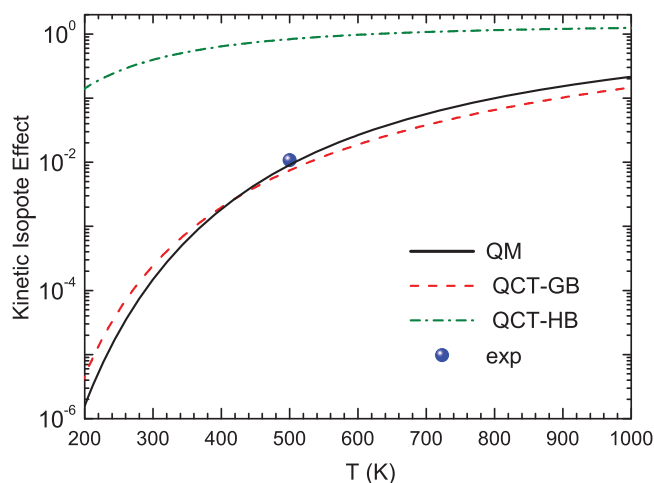


FIG. 4. Kinetic isotope effect,  $k_{\text{Mu}}(T)/k_{\text{He}\mu}(T)$ . Symbols and lines as in Fig. 1. The experimental point (blue solid circle) is taken from Ref. 10.

differences in the quantized levels of the two transition states. However, the QCT-GB results, which do not contemplate an explicit quantization of the transition state, can describe the experimental data fairly well, and are in good agreement with QM calculations. It seems thus that just a realistic consideration of the ZPE of the products, such as that implied in the GB procedure, can account essentially for the measured  $k(T)$ , notably in the  $\text{Mu} + \text{H}_2$  reaction, and can justify the observed KIE. It may appear surprising that the QCT calculations, which do not consider tunneling, can reproduce well the QM and experimental results. In the case of the  $\text{He}\mu + \text{H}_2$  reaction, Fleming *et al.* showed that tunneling is indeed relevant in correcting the variational transition state rate coefficients (see Fig. 2 of Ref. 10). However, as pointed out in previous works,<sup>26,41-43</sup> the neglect of both ZPE and tunneling at the barrier in the QCT method could result in cancellation of errors that would lead to good agreement with QM and with experiment. This seems to be the case for the  $\text{He}\mu + \text{H}_2$  reaction (see Fig. 2), where the deviations between the QCT and QM data only become truly appreciable at low temperatures. Indeed, a similar behavior was obtained for other isotopic variants of the  $\text{H}_3$  reaction.<sup>18,26</sup> In the case of the  $\text{Mu} + \text{H}_2$ , one would expect the effect of tunneling to be paramount given the small mass of the Mu isotopologue. However, as discussed in Ref. 10, the effective tunneling barrier is much broader for this reaction than for any other isotopic variant of the  $\text{H}_3$  system due to the extremely high ZPE of the MuH product. Therefore, in the reaction of  $\text{Mu} + \text{H}_2$ , the possible effects of tunneling are largely superseded by the influence of the large ZPE.

Within a purely classical framework, the *total energy threshold* for the series of  $\text{X} + \text{H}_2$  reactions ( $\text{X} = \text{Mu}, \text{H}, \text{D}, \text{He}\mu$ ) is primarily governed by the height of the classical barrier,  $E_b = 0.4169$  eV, and to a lesser extent by the ability of reactant's vibrational energy to help overcome the barrier.<sup>9</sup> It is found that this ability declines with decreasing mass of the attacking atom; i.e., the QCT-HB threshold, which would be the same if it were just governed by the energetics, decreases somewhat from  $\text{Mu} + \text{H}_2$  to  $\text{He}\mu + \text{H}_2$ . It was also found<sup>9</sup>

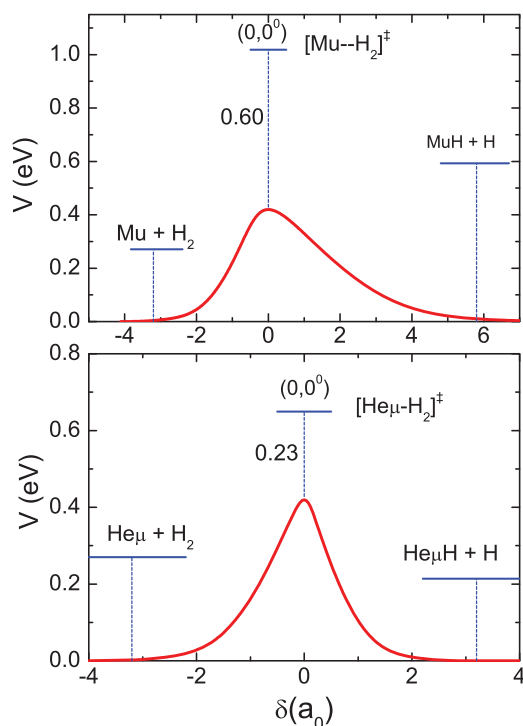


FIG. 5. Minimum energy path for the  $\text{Mu} + \text{H}_2$  (top) and  $\text{He}\mu + \text{H}_2$  (bottom) representing the potential vs the mass scaled reaction coordinate. The differences between the two diagrams are apparent. Because of the very high ZPE of the  $\text{MuH}$  molecule (above the classical barrier), tunneling through the effective reaction barrier is much less effective than in the  $\text{He}\mu + \text{H}_2$ .

that the post-threshold reactivity grows with the size of the attacking atom. In this way, these two effects are a manifestation of a classical quasi-adiabaticity, preserving a significant fraction of the initial vibrational energy from the reactants to the products as the reaction proceeds. Its QM counterpart would be the quantization of the transition state. However, as can be appreciated in Fig. 5, for the endoergic  $\text{Mu} + \text{H}_2$  reaction, the actual threshold is dominated by the extremely high ZPE energy of  $\text{MuH}$  (0.5930 eV), which lies above the classical barrier. In the end, this higher threshold would be at the root of the small rate coefficients for the  $\text{Mu} + \text{H}_2$  reaction. In the QCT-HB results, which neglect the quantization of  $\text{MuH}$ , the calculated  $k(T)$  is only somewhat smaller than that of the rest of possible isotopic variants; as a result, the corresponding HB KIE is close to one over most of the temperature range considered (see Fig. 4). For other isotopic variants of  $\text{H} + \text{H}_2$  not involving a  $\text{Mu}$  atom, the product's ZPE lies below the classical barrier, as shown in Fig. 5 for the case of the reaction with  $\text{He}\mu$ . Consequently, their reaction thresholds are similar and the constraint of the product's ZPE is much less demanding (the reactions are exothermic or thermoneutral). As a result, a pronounced KIE with respect to  $\text{Mu} + \text{H}_2$  can also be expected for other isotopic variants of this reaction. As an example, we can take the ratio  $k_{\text{Mu}}/k_{\text{D}}$  between the experimental rate coefficients of  $\text{Mu} + \text{H}_2$  and  $\text{D} + \text{H}_2$ , which takes a value of 0.014 at 500 K,<sup>12,40</sup> not much larger than the 0.011 value discussed above for the reactions of  $\text{Mu} + \text{H}_2$  and  $\text{He}\mu + \text{H}_2$ .

## IV. CONCLUSIONS

In the present work, extensive QCT and accurate QM calculations have been carried out in order to determine the thermal rate coefficients and KIE of the  $\text{Mu} + \text{H}_2$  and  $\text{He}\mu + \text{H}_2$  reactions. A general good agreement has been found between the QM data and those obtained with the QCT method when the Gaussian binning procedure for the assignment of final states is applied.

We conclude that although the influence of distinct quantized transition states can explain the marked KIE reported for the reactions of  $\text{Mu}$  and  $\text{He}\mu$  with  $\text{H}_2$ ,<sup>10</sup> results based on classical dynamics, without explicitly invoking a quantization of the transition state, can also account for the data as long as constraints are set to preserve the products' ZPE. These constraints, effected by the Gaussian binning procedure, may preferentially filter vibrationally adiabatic trajectories, resulting in a sort of classical analog of the quantized transition state. Within this picture, the high zero point energy of the  $\text{MuH}$  product molecule would be the determinant factor for the observed kinetic isotope effect.

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