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# Accurate ab initio potential energy surface, thermochemistry, and dynamics of the Br(2P, 2P3/2) + CH4 $\rightarrow$ HBr + CH3 reaction

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#### ADVERTISEMENT





## Accurate *ab initio* potential energy surface, thermochemistry, and dynamics of the Br( ${}^{2}P, {}^{2}P_{3/2}$ ) + CH<sub>4</sub> $\rightarrow$ HBr + CH<sub>3</sub> reaction

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Chemically accurate full-dimensional non-spin-orbit and spin-orbit (SO) ground-state potential energy surfaces (PESs) are obtained for the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction by fitting 21 574 composite *ab initio* energy points. The composite method considers electron correlation methods up to CCSD(T), basis sets up to aug-cc-pwCVTZ-PP, correlation of the core electrons, scalar relativistic effects via an effective core potential (ECP), and SO corrections, thereby achieving an accuracy better than 0.5 kcal/mol. Benchmark structures and relative energies are computed for the stationary points using the *ab initio* focal-point analysis (FPA) scheme based on both ECP and Douglas-Kroll approaches providing all-electron relativistic CCSDT(Q)/complete-basis-set quality energies. The PESs accurately describe the saddle point of the abstraction reaction and the van der Waals complexes in the entrance and product channels. The SO-corrected PES provides a classical barrier height of 7285(7232  $\pm$  50) cm<sup>-1</sup>,  $D_{\rm e}$  values of 867(799  $\pm$  10) and 399(344  $\pm$  10) cm<sup>-1</sup> for the complexes CH<sub>3</sub>-HBr and CH<sub>3</sub>-BrH, respectively, and reaction endothermicity of 7867(7857  $\pm$  50) cm<sup>-1</sup>, in excellent agreement with the new, FPA-based benchmark data shown in parentheses. The difference between the Br + CH<sub>4</sub> asymptotes of the non-SO and SO PESs is 1240 cm<sup>-1</sup>. in good agreement with the experiment (1228 cm<sup>-1</sup>). Quasiclassical trajectory calculations based on more than 13 million trajectories for the late-barrier Br + CH<sub>4</sub>( $v_k = 0, 1$ ) [k = 1, 2, 3, 4] reactions show that the vibrational energy, especially the excitation of the stretching modes, activates the reaction much more efficiently than translational energy, in agreement with the extended Polanyi rules. Angular distributions show dominant backward scattering for the ground-state reaction and forward scattering for the stretching-excited reactions. The reactivity on the non-SO PES is about 3-5 times larger than that on the SO PES in a wide collision energy range of 8000-16000 cm<sup>-1</sup>. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4797467]

#### I. INTRODUCTION

Accurate dynamical simulations of chemical reactions began with computations for  $A + BC \rightarrow AB + C$  reactions. Solution of the electronic Schrödinger equation at fixed nuclear configurations provides the points of the Born-Oppenheimer (BO) potential energy surface (PES), on which the chemical reaction occurs. The early dynamical studies on the triatomic A + BC systems found that the location of the barrier on the PES, which separates the reactants from the products, determines many details of the reaction dynamics. This observation led to the rules of thumb of reaction dynamics. These rules, now called Polanyi rules,<sup>1</sup> predict that vibrational energy is more efficient than translational energy to activate the late-barrier bimolecular reactions, and the reverse is true for early-barrier reactions. Chemists began to extend the studies of A + BC systems by replacing the diatomic BC with tri-(H<sub>2</sub>O),<sup>2-4</sup> tetra-(NH<sub>3</sub>),<sup>5</sup> and penta-atomic  $(CH_4)^{6-11}$  molecules. As the systems become more complex, the extension of the Polanyi rules may be problematic due to the increasing number of vibrational degrees of freedom. The theoretical simulation of polyatomic reactions also becomes challenging due to the high dimensionality of the PES. Recent advances in the representation of PESs of high dimensionality allow developing chemically accurate PESs for six-atom reactions based on fitting a moderate number of *ab initio* electronic energies.<sup>12,13</sup> In the past 4 years we developed high-quality *ab initio* PESs for the  $X + CH_4$ reactions, where X is F, Cl, and O.14-17 Quasiclassical and quantum dynamical computations<sup>14, 15, 17-20</sup> on these PESs supported and explained most of the available experimental findings<sup>8,21–23</sup> and predicted results that inspired experimental reinvestigations<sup>24</sup> and may inspire future measurements. For  $H + H_2O/HDO$  the Polanyi rules seem to work well, but recent experiments and computations on the  $F + H_2O$  reaction<sup>25</sup> and the more complex  $X + CH_4$  reactions found that the dynamics do not always follow our chemical expectations, e.g., CH stretching excitation enhances the D abstraction channel in the  $F + CHD_3$  reaction.<sup>8</sup> Clearly, more experimental and theoretical studies are needed to get a deeper understanding of the dynamics of polyatomic chemical reactions.

The present study focuses on the  $Br + CH_4 \rightarrow HBr + CH_3$  reaction complementing the previous work on F, O, and Cl + CH<sub>4</sub> systems. The shapes of the PESs of these X + CH<sub>4</sub> reactions are significantly different; thus, we can expect to gain new insight into the dynamics of

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polyatomic reactions by varying X from F to Br. The location of the barrier shifts from reactant-like to product-like for F (early barrier and very exothermic), O (central barrier and slightly endothermic), Cl (late barrier and slightly endothermic), and Br (late barrier and very endothermic), in order. The  $Br + CH_4$  reaction has the unique feature that the saddle point and the HBr + CH<sub>3</sub> asymptote have nearly the same energy. Many theoretical and experimental studies show that the rate constants of the HBr + CH<sub>3</sub> reaction have a strong nonlinear Arrhenius behavior and negative temperature dependence at lower temperatures,<sup>26–28</sup> but the detailed explanation of the kinetics is still an open question. There are a lot of contradictions in the literature about the sign of the saddle-point energy relative to HBr + CH<sub>3</sub> and the existence/stability of a CH<sub>3</sub>-HBr complex. which may or may not affect the dynamics and kinetics of the  $HBr + CH_3$  reaction. Theoretical studies based on Gaussian-1 theory,<sup>29</sup> all-electron UMP2/6-311G(3df,d,p),<sup>26</sup> and frozen-core CCSD(T)/cc-pVTZ +  $BSSE^{30}$  found a *positive* vibrationally adiabatic ground state barrier height, whereas a slightly negative barrier was predicted by QCISD(T)/6-311++G(3df,3pd)//QCISD/6-311G(2df,2p),<sup>31</sup> MP4/6-311 ++G(3df,3pd)//QCISD/6-31+G(d),<sup>27</sup> and frozen-core ECP-RCCSD(T)/cc-pVnZ-PP//QCISD/6-311G(d,p) extrapolated to the complete basis set (CBS) using n = 2-4.<sup>28</sup>

In the present study we finally resolve the contradictions by employing the state-of-the-art *ab initio* focal-point analysis (FPA) technique,<sup>32,33</sup> thereby improving the accuracy and reducing the uncertainty concerning the energetics of the title reaction. The FPA systematically improves the level of the electron correlation methods, the size of the basis sets, and considers relativistic effects, thereby approaching the relativistic all-electron full-configuration-interaction/completebasis-set limit<sup>34</sup> and providing good estimates for the uncertainties of the final results. To work with experimentally relevant quantities, zero-point vibrational energy (ZPE) corrections are added to the purely theoretical equilibrium values. The FPA for the title reaction employs correlation methods up to all-electron CCSDT(Q), basis sets up to augcc-pwCV5Z allowing accurate extrapolation to the CBS limit, scalar relativistic, spin-orbit (SO), and ZPE corrections. Since the title reaction involves a heavy atom (Br) we pay special attention to the core-core and core-valence correlation effects as well as the scalar relativistic effects by comparing two alternative methods based on either effective core potentials (ECP) or Douglas-Kroll (DK) relativistic one-electron integrals.

Following the early PES developments based on reduced-dimensional *ab initio*<sup>26</sup> and full-dimensional semiempirical<sup>30</sup> methods, we report here the first full-dimensional *ab initio* PES for the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction. We employ the permutationally invariant polynomial approach<sup>12,13</sup> to fit a large number of accurate composite *ab initio* energies. The composite method considers electron correlation up to all-electron CCSD(T), basis sets up to augcc-pwCVTZ-PP, scalar relativity based on ECP, and SO effects at the all-electron ECP-MRCI+Q/aug-cc-pwCVDZ-PP level of theory. We show the accuracy and efficiency of this composite method by comparing to various *ab initio* levels of theory. The structures, harmonic vibrational frequencies, and energies of the stationary points of the PES are calculated and compared to the new benchmark data.

The new analytical PES opens the door for many dynamical investigations both for the Br + CH<sub>4</sub> and HBr + CH<sub>3</sub> reactions. In this paper we focus on the mode-selective dynamics of the Br + CH<sub>4</sub> reaction. Quasiclassical trajectory (QCT) calculations are performed for the reactant groundstate, bending-excited, and stretching-excited Br( $^{2}P_{3/2}$ ) + CH<sub>4</sub> reactions at different collision energies. We compare the QCT results with previous findings on other X + CH<sub>4</sub> reactions, which may extend our chemical knowledge on modeselective polyatomic reactivity.

#### II. BENCHMARK AB INITIO CHARACTERIZATION

#### A. Computational details

Due to significant scalar relativistic and core correlation effects in the  $Br + CH_4$  system we consider various *ab* initio methods and basis sets to achieve high accuracy and get some insight about the uncertainty of the applied methods. The non-relativistic frozen-core computations employ the correlation-consistent polarized Valence n-Zeta basis sets augmented with diffuse functions denoted aug-cc-pVnZ [n= 2(D), 3(T), 4(Q).<sup>35</sup> Relativistic ECP computations replace the inner core  $1s^2 2s^2 2p^6$  electrons of the Br atom by the smallcore energy-consistent pseudopotential of the Stuttgart/Köln type<sup>36</sup> and treat the other 25 electrons  $(3s^23p^63d^{10}4s^24p^5)$ of the Br atom explicitly. The usual frozen-core (FC) approach does not correlate the  $3s^23p^63d^{10}$  electrons of Br and the  $1s^2$  electrons of the C atom. In the all-electron (AE) computations all the explicitly treated electrons are correlated. For the FC-ECP computations the aug-cc-pVnZ-PP [n= 2(D), 3(T), 4(Q) basis sets<sup>36</sup> are used, where PP denotes that the basis for Br was optimized for ECP computations, whereas the usual aug-cc-pVnZ functions are used for C and H. For AE-ECP computations we use the aug-cc-pwCVnZ-PP [n = 2(D), 3(T), 4(Q), 5] basis sets,<sup>37</sup> where C denotes tight functions designed to describe the core electron correlation. We also employ an alternative relativistic method based on relativistic one-electron integrals using the second-order Douglas-Kroll-Hess Hamiltonian.<sup>38</sup> For the AE-DK computations we employ the aug-cc-pwCVnZ-DK [n = 2(D), 3(T), 4(Q), 5] basis sets<sup>39</sup> optimized for DK calculations. Here, AE means that only the inner core electrons  $(1s^22s^22p^6)$ of the Br atom are kept frozen and all the outer core electrons of Br  $(3s^23p^63d^{10})$  and the core electrons of C  $(1s^2)$  as well as all the valence electrons are correlated.

We employ the following single-reference correlation methods: second-order Møller–Plesset perturbation theory (MP2)<sup>40</sup> and a series of coupled-cluster (CC)<sup>41</sup> methods such as CCSD,<sup>42</sup> CCSD(T),<sup>43</sup> CCSDT,<sup>44</sup> CCSDT(Q),<sup>45</sup> where S, D, and T denote all the single, double, and triple excitations and (T) and (Q) mean the perturbative treatment of triple and quadruple excitations. For open-shell systems both the restricted and unrestricted open-shell MP2, denoted as RMP2 and UMP2, respectively, are employed. The CC methods utilize unrestricted formalism, denoted UCC, and restricted open-shell Hartree–Fock (ROHF) reference for

UCCSD and UCCSD(T) and unrestricted HF (UHF) orbitals for UCCSDT and UCCSDT(Q). The multi-reference configuration interaction (MRCI+Q)<sup>46</sup> computations using the Davidson correction<sup>47</sup> to estimate the effect of the higherorder excitations (+Q) utilize an active space of 5 electrons in the 3 spatial 4*p*-like orbitals corresponding to Br. The spin-orbit calculations employ the Breit–Pauli operator in the interacting states approach.<sup>48</sup> All the *ab initio* computations are performed using MOLPRO,<sup>49</sup> except UCCSDT and UCCSDT(Q), for which the MRCC program<sup>50,51</sup> (interfaced to MOLPRO) is employed.

We use both the ECP and DK methods to perform the benchmark FPA analysis<sup>32, 33</sup> using the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP and AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK reference structures, respectively. Single-point AE-ECP and AE-DK computations are performed by ROHF, RMP2, UCCSD, and UCCSD(T) with the basis sets aug-cc-pwCVnZ-PP/aug-cc-pwCVnZ-DK [n = 2(D), 3(T), 4(Q), 5] and the electron correlation beyond UCCSD(T) is estimated as the difference between FC-ECP-UCCSD(T)/aug-cc-pVnZ-PP and FC-ECP-UCCSDT(Q)/aug-cc-pVnZ-PP energies with n = D or T. The ROHF energies,  $E_n^{\rm HF}$ , are extrapolated to the CBS limit,  $E_{\rm CBS}^{\rm HF}$ , using<sup>52</sup>

$$E_n^{\rm HF} = E_{\rm CBS}^{\rm HF} + a(n+1)e^{-9\sqrt{n}}.$$
 (1)

For the all-electron RMP2, UCCSD, and UCCSD(T) correlation energy increments,  $E_n^{\text{corr.}}$ , the CBS limits,  $E_{\text{CBS}}^{\text{corr.}}$ , are obtained by the extrapolation formula<sup>53</sup>

$$E_n^{\text{corr.}} = E_{\text{CBS}}^{\text{corr.}} + bn^{-3}.$$
 (2)

In order to get the best estimates for the CBS limits using the above two-parameter asymptotic formulas, the best two energies, i.e., n = 4 and 5, are used in the extrapolations. The scalar relativistic effects are incorporated in both the ECP and DK computations. The final FPA results are obtained by taking the average value of the ECP and DK results and the slight differences between the two approaches are taken into account in the uncertainties. The SO corrections are obtained from the experimentally known SO splitting of the Br atom. The harmonic ZPE corrections are computed at the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP level of theory, except for the reaction enthalpy for which AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP harmonic as well as variationally computed anharmonic ZPE corrections are employed.

#### B. The Br–CH<sub>4</sub> van der Waals region

The ground electronic state of the Br atom (<sup>2</sup>P) is split into the fourfold degenerate SO ground state (<sup>2</sup>P<sub>3/2</sub>) and the twofold degenerate excited SO state (<sup>2</sup>P<sub>1/2</sub>). The best experimental value for the splitting is  $\varepsilon = 3685$  cm<sup>-1</sup>; thus, the SO ground state is below the non-SO state by  $\varepsilon/3 = 1228$  cm<sup>-1</sup>. The Br(<sup>2</sup>P<sub>1/2</sub>) is non-reactive within the BO approximation. When Br(<sup>2</sup>P<sub>3/2</sub>) approaches CH<sub>4</sub> the fourfold degenerate SO state splits into two doubly degenerate SO states and only one of them correlates with electronically ground-state products. Thus, three doubly degenerate SO states are involved in the dynamics of the Br + CH<sub>4</sub> reaction, and only the SO ground state is reactive within an adiabatic approach. Potential energy curves have been computed for Br-CH<sub>4</sub> as a function of the C-Br distance at the FC-ECP-MRCI+Q/augcc-pVnZ-PP and AE-ECP-MRCI+Q/aug-cc-pwCVnZ-PP [n = D and T] levels of theory. The former gives splittings of 3531 and 3564 cm<sup>-1</sup> with n = D and T, respectively, whereas the latter gives 3747 and 3846 cm<sup>-1</sup> with n = D and T, respectively. Based on the best agreement between theory and experiment, i.e.,  $3685 \text{ cm}^{-1} \text{ vs.} 3747 \text{ cm}^{-1}$ , we show the AE-ECP-MRCI+Q/aug-cc-pwCVDZ-PP potential curves in Fig. 1. As seen, the potentials depend on the orientation of CH<sub>4</sub> relative to Br. We consider two different orientations with CH-Br and HC-Br linear bond arrangements (see the structures in Fig. 1). There is a shallow van der Waals (vdW) well in the entrance channel of the  $Br + CH_4$  reaction. The position and depth of this well depend on the orientation of the CH<sub>4</sub> fragment. On the non-SO ground state the minima occur at about 4.0 and 3.5 Å C-Br distances for CH-Br and HC-Br complexes, respectively. The latter is significantly deeper, since the depths are 211/97 and 384/268  $cm^{-1}$  for the CH–Br and HC-Br minima, respectively, obtained with the aug-ccpwCVDZ-PP/aug-cc-pwCVTZ-PP bases. The SO coupling shifts the location of the above minima to 4.2 and 3.7 Å, respectively. The SO effect on the depths is minor for the CH–Br complex, since 211/97 cm<sup>-1</sup> becomes 197/100 cm<sup>-1</sup>, whereas the HC-Br minimum is significantly shallower on the SO ground state  $(290/193 \text{ cm}^{-1})$  than on the non-SO potential  $(384/268 \text{ cm}^{-1})$ . Note that the non-reactive HC–Br minimum remains the deeper minimum on the SO ground-state potential, as well. As seen from the above data, the basis set effect is huge on the depths; as expected, the aug-cc-pwCVDZ-PP basis gives too deep minima. On the basis of the detailed analysis performed previously for the similar  $Cl + CH_4$  reaction considering both MRCI+Q and CCSD(T) methods and basis sets as large as aug-cc-pCVQZ with and without counterpoise correction for the basis set superposition error, we can be confident that the present AE-ECP-MRCI+Q/aug-cc-pwCVTZ-PP data for the well depths are accurate.<sup>16</sup> It is interesting to note that the vdW well, depths and positions of the minima, of the  $Br + CH_4$  reaction is very similar to that of the Cl  $+ CH_4$  reaction.<sup>16</sup>

### C. Structures of the saddle point and the CH<sub>3</sub>–HBr and CH<sub>3</sub>–BrH complexes

Structures of the first-order saddle point, complexes in the HBr + CH<sub>3</sub> channel, and the reactants and products computed at various levels of theory are given in Tables I–III, respectively. The Br + CH<sub>4</sub> reaction has a late barrier, i.e., the saddle-point structure is similar to that of the products. Indeed, the C–H<sub>b</sub>, where H<sub>b</sub> is connected to Br, distance is 1.67 Å, stretched substantially, by 0.58 Å, relative to the bond length in CH<sub>4</sub>. On the other hand, the H<sub>b</sub>–Br distance is 1.49 Å, stretched by only 0.07 Å relative to the bond length in the HBr molecule. The CH bond length within the CH<sub>3</sub> unit at the saddle point is contracted and stretched by 0.007 and 0.003 Å relative to the equilibrium CH bond lengths in CH<sub>4</sub> and CH<sub>3</sub>, respectively. This is also consistent with the product-like barrier of the Br + CH<sub>4</sub> reaction. The UMP2



FIG. 1. Potential energy curves for the entrance channel of the  $Br + CH_4$  reaction as a function of the C–Br distance along the  $C_3$  axis with fixed CH<sub>4</sub>(eq) geometry. The left panels show the direct *ab initio* results obtained at the AE-ECP-MRCI+Q/aug-cc-pwCVDZ-PP level of theory, whereas the right panels show the one-dimensional cuts of the non-SO and SO PESs. A<sub>1</sub> and E denote the non-SO ground and excited electronic states, respectively, and SO<sub>1</sub>, SO<sub>2</sub>, and SO<sub>3</sub> are the three SO states.

method significantly underestimates the C–H<sub>b</sub> distance by about 0.07 Å relative to the high-quality UCCSD(T) results. For the other structural parameters the differences between the UMP2 and UCCSD(T) results are less significant; i.e., about 0.002–0.005 Å for the H<sub>b</sub>–Br and CH distances. The AE-ECP and AE-DK computations usually provide the same structural data, except for the C–H<sub>b</sub> distance, where the differences are 0.009, 0.003, and 0.001 Å with n = D, T, and Q bases, respectively. It is comforting to see that the ECP and DK results approach each other as the basis size increases.

We have found two minima in the HBr + CH<sub>3</sub> channel; a deeper one with CH<sub>3</sub>–H<sub>b</sub>Br orientation and a shallower one with CH<sub>3</sub>–BrH<sub>b</sub> connectivity. Both complexes have  $C_{3v}$  pointgroup symmetry. The C–H<sub>b</sub> distance for the former is 2.18 Å, stretched by 0.51 Å relative to the saddle-point value. The C–Br distance in the latter complex is 3.44 Å, i.e., significantly longer than the C–H<sub>b</sub> distance in CH<sub>3</sub>–H<sub>b</sub>Br. Clearly, the CH<sub>3</sub>–BrH<sub>b</sub> complex is more product-like, since the H<sub>b</sub>– Br distance is stretched by only 0.002 Å relative to HBr, whereas in CH<sub>3</sub>–H<sub>b</sub>Br the H<sub>b</sub>–Br distance is longer than the HBr bond length by 0.013 Å. Furthermore, the HCH<sub>b</sub> angles are 93.0° and 90.4° for the complexes CH<sub>3</sub>–H<sub>b</sub>Br and CH<sub>3</sub>–BrH<sub>b</sub>, respectively; thus, these angles are closer and closer to 90°, in order. The UMP2 method gives reasonable estimates for these structures, since the inter-fragment separations at the UCCSD(T) levels are just slightly longer, by about 0.02–0.05 Å, than the corresponding UMP2 results. The AE-ECP and AE-DK methods give very similar results; the AE-DK inter-fragment distances are shorter by only about 0.004–0.006 Å than the AE-ECP results. The basis set effects are found to be significant for CH<sub>3</sub>–H<sub>b</sub>Br, because the n = D basis sets overestimate the C–H<sub>b</sub> separation by about 0.07–0.09 Å, whereas for the CH<sub>3</sub>–BrH<sub>b</sub> complex the basis set effects are only about 0.01 Å.

#### D. Barrier height, dissociation energies, and reaction enthalpy

Benchmark barrier height, dissociation energies of CH<sub>3</sub>– HBr and CH<sub>3</sub>–BrH, and reaction enthalpy have been computed using the FPA approach as described in Sec. II A. In the discussion below, we use the DZ, TZ, QZ, and 5Z simplified notations for the aug-cc-pwCV*n*Z-PP/aug-cc-pwCV*n*Z-DK basis sets with n = D, T, Q, and 5, respectively. Furthermore,  $\delta$ [RMP2],  $\delta$ [UCCSD],  $\delta$ [UCCSD(T)],  $\delta$ [UCCSDT], and  $\delta$ [UCCSDT(Q)] denote all-electron correlation energy increments with respect to the preceding level of theory; i.e.,

TABLE I. Structure (in Å and degrees;  $C_{3v}$  symmetry) and non-SO classical barrier height ( $V_{SP}$ , cm<sup>-1</sup>) for the saddle point (CH<sub>3</sub>-H<sub>b</sub>-Br)<sub>SP</sub> at different levels of theory.

Methods <sup>a</sup>	r(CH)	<i>r</i> (CH <sub>b</sub> )	<i>r</i> (H <sub>b</sub> Br)	$\alpha(\text{HCH}_{b})$	V <sub>SP</sub>
FC-UMP2/aug-cc-pVDZ	1.091	1.607	1.511	98.1	6251
FC-UMP2/aug-cc-pVTZ	1.079	1.601	1.503	98.2	6306
FC-UMP2/aug-cc-pVQZ	1.077	1.598	1.503	98.0	6187
FC-ECP-UMP2/aug-cc-pVDZ-PP	1.091	1.634	1.503	97.8	6443
FC-ECP-UMP2/aug-cc-pVTZ-PP	1.079	1.617	1.495	98.0	6489
FC-ECP-UMP2/aug-cc-pVQZ-PP	1.077	1.615	1.495	97.8	6354
AE-ECP-UMP2/aug-cc-pwCVDZ-PP	1.090	1.619	1.496	97.8	5966
AE-ECP-UMP2/aug-cc-pwCVTZ-PP	1.077	1.605	1.489	98.0	6031
AE-ECP-UMP2/aug-cc-pwCVQZ-PP	1.076	1.605	1.489	97.8	5925
AE-DK-UMP2/aug-cc-pwCVDZ-DK	1.090	1.610	1.496	97.9	5823
AE-DK-UMP2/aug-cc-pwCVTZ-DK	1.077	1.602	1.489	98.0	5886
AE-DK-UMP2/aug-cc-pwCVQZ-DK	1.075	1.604	1.489	97.8	5879
FC-UCCSD(T)/aug-cc-pVDZ	1.096	1.663	1.507	97.7	6055
FC-UCCSD(T)/aug-cc-pVTZ	1.083	1.668	1.498	97.6	6221
FC-UCCSD(T)/aug-cc-pVQZ	1.081	1.666	1.498	97.4	6109
FC-ECP-UCCSD(T)/aug-cc-pVDZ-PP	1.096	1.689	1.500	97.4	6253
FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP	1.082	1.687	1.491	97.4	6402
FC-ECP-UCCSD(T)/aug-cc-pVQZ-PP	1.081	1.686	1.491	97.2	6271
AE-ECP-UCCSD(T)/aug-cc-pwCVDZ-PP	1.095	1.677	1.494	97.5	6009
AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP	1.081	1.674	1.486	97.4	6219
AE-DK-UCCSD(T)/aug-cc-pwCVDZ-DK	1.095	1.668	1.494	97.5	5892
AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK	1.081	1.671	1.486	97.5	6079

<sup>a</sup>FC and AE denote frozen-core and all-electron computations, respectively. ECP computations employ effective core potential for Br and DK means using the second-order Douglas-Kroll relativistic method.

TABLE II.	Equilibrium structures (in Å and degrees)	and dissociation energies (De, cm	<sup>-1</sup> ) of the complexes CH <sub>3</sub> –HBr a	and CH3-BrH at different levels of
theory.				

	$CH_3$ – $H_bBr(C_{3v})$					$CH_3$ – $BrH_b$ ( $C_{3v}$ )				
Methods <sup>a</sup>	r(CH)	r(CH <sub>b</sub> )	r(H <sub>b</sub> Br)	$\alpha(\text{HCH}_{b})$	De	r(CH)	r(CBr)	r(BrH <sub>b</sub> )	$\alpha$ (HCBr)	De
FC-UMP2/aug-cc-pVDZ	1.089	2.242	1.434	92.9	918	1.088	3.474	1.424	90.4	402
FC-UMP2/aug-cc-pVTZ	1.076	2.171	1.429	93.1	880	1.075	3.478	1.417	90.4	344
FC-UMP2/aug-cc-pVQZ	1.075	2.166	1.429	93.0	849	1.074	3.462	1.416	90.4	342
FC-ECP-UMP2/aug-cc-pVDZ-PP	1.089	2.218	1.435	93.0	927	1.088	3.477	1.424	90.4	395
FC-ECP-UMP2/aug-cc-pVTZ-PP	1.076	2.155	1.428	93.3	884	1.075	3.444	1.415	90.4	372
FC-ECP-UMP2/aug-cc-pVQZ-PP	1.075	2.153	1.428	93.0	855	1.074	3.428	1.414	90.4	365
AE-ECP-UMP2/aug-cc-pwCVDZ-PP	1.088	2.204	1.427	93.0	959	1.087	3.450	1.416	90.4	424
AE-ECP-UMP2/aug-cc-pwCVTZ-PP	1.075	2.139	1.420	93.2	909	1.074	3.416	1.407	90.4	386
AE-ECP-UMP2/aug-cc-pwCVQZ-PP	1.073	2.137	1.421	93.0	879	1.072	3.404	1.407	90.4	379
AE-DK-UMP2/aug-cc-pwCVDZ-DK	1.088	2.213	1.424	92.9	970	1.087	3.434	1.413	90.4	439
AE-DK-UMP2/aug-cc-pwCVTZ-DK	1.074	2.135	1.420	93.2	942	1.073	3.412	1.406	90.4	395
AE-DK-UMP2/aug-cc-pwCVQZ-DK	1.073	2.133	1.421	93.0	884	1.072	3.407	1.407	90.4	376
FC-UCCSD(T)/aug-cc-pVDZ	1.094	2.278	1.438	92.7	881	1.093	3.475	1.430	90.4	402
FC-UCCSD(T)/aug-cc-pVTZ	1.081	2.192	1.434	93.0	836	1.080	3.490	1.423	90.4	339
FC-UCCSD(T)/aug-cc-pVQZ	1.079	2.198	1.434	92.8	797	1.078	3.475	1.423	90.4	333
FC-ECP-UCCSD(T)/aug-cc-pVDZ-PP	1.094	2.255	1.439	92.8	894	1.094	3.477	1.430	90.4	396
FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP	1.081	2.183	1.433	93.0	837	1.080	3.456	1.421	90.4	366
FC-ECP-UCCSD(T)/aug-cc-pVQZ-PP	1.079	2.187	1.432	92.9	801	1.078	3.442	1.421	90.4	354
AE-ECP-UCCSD(T)/aug-cc-pwCVDZ-PP	1.093	2.253	1.431	92.7	909	1.092	3.457	1.423	90.4	419
AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP	1.079	2.184	1.426	93.0	840	1.078	3.440	1.415	90.4	369
AE-DK-UCCSD(T)/aug-cc-pwCVDZ-DK	1.093	2.264	1.428	92.7	912	1.092	3.442	1.421	90.4	430
AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK	1.079	2.178	1.426	93.0	874	1.078	3.436	1.414	90.4	378

<sup>a</sup>FC and AE denote frozen-core and all-electron computations, respectively. ECP computations employ effective core potential for Br and DK means using the second-order Douglas-Kroll relativistic method.

TABLE III. Equilibrium structures (in Å and degrees) of the reactants and products and the vibrationless enthalpy ( $\Delta E_e$ , cm<sup>-1</sup>) of the Br(<sup>2</sup>P) + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction at different levels of theory.

	$Br + CH_4$		$\mathrm{HBr} + \mathrm{CH}_3 \left( D_{3\mathrm{h}} \right)$			
Methods <sup>a</sup>	r(CH)	r(CH)	r(HBr)	$\Delta E_{\rm e}$		
FC-UMP2/aug-cc-pVDZ	1.098	1.088	1.423	6746		
FC-UMP2/aug-cc-pVTZ	1.086	1.075	1.415	6832		
FC-UMP2/aug-cc-pVQZ	1.085	1.073	1.415	6687		
FC-ECP-UMP2/aug-cc-pVDZ-PP	1.098	1.088	1.423	7041		
FC-ECP-UMP2/aug-cc-pVTZ-PP	1.086	1.075	1.413	7073		
FC-ECP-UMP2/aug-cc-pVQZ-PP	1.085	1.073	1.412	6917		
AE-ECP-UMP2/aug-cc-pwCVDZ-PP	1.097	1.087	1.414	6598		
AE-ECP-UMP2/aug-cc-pwCVTZ-PP	1.084	1.073	1.405	6639		
AE-ECP-UMP2/aug-cc-pwCVQZ-PP	1.083	1.072	1.405	6519		
AE-DK-UMP2/aug-cc-pwCVDZ-DK	1.097	1.086	1.411	6436		
AE-DK-UMP2/aug-cc-pwCVTZ-DK	1.084	1.073	1.405	6523		
AE-DK-UMP2/aug-cc-pwCVQZ-DK	1.083	1.072	1.405	6479		
FC-UCCSD(T)/aug-cc-pVDZ	1.103	1.093	1.429	6570		
FC-UCCSD(T)/aug-cc-pVTZ	1.090	1.080	1.421	6801		
FC-UCCSD(T)/aug-cc-pVQZ	1.088	1.078	1.421	6648		
FC-ECP-UCCSD(T)/aug-cc-pVDZ-PP	1.103	1.093	1.429	6870		
FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP	1.090	1.080	1.420	7029		
FC-ECP-UCCSD(T)/aug-cc-pVQZ-PP	1.088	1.078	1.419	6861		
AE-ECP-UCCSD(T)/aug-cc-pwCVDZ-PP	1.101	1.092	1.421	6619		
AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP	1.088	1.078	1.413	6824		
AE-ECP-UCCSD(T)/aug-cc-pwCVQZ-PP	1.087	1.076	1.413	6705		
AE-DK-UCCSD(T)/aug-cc-pwCVDZ-DK	1.101	1.092	1.419	6472		
AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK	1.088	1.078	1.412	6716		
AE-DK-UCCSD(T)/aug-cc-pwCVQZ-DK	1.086	1.076	1.413	6675		

<sup>a</sup>FC and AE denote frozen-core and all-electron computations, respectively. ECP computations employ effective core potential for Br and DK means using the second-order Douglas-Kroll relativistic method.

RMP2 results relative to ROHF results, UCCSD relative to RMP2, etc.

The FPA results for the classical barrier height  $(V_{SP})$  of the Br + CH<sub>4</sub> reaction are given in Table IV. The ROHF method seriously overestimates the barrier height by about 60%. As expected, the ROHF energies converge rapidly and the 5Z result is just below the CBS  $V_{SP}$  by only 1 cm<sup>-1</sup>. The ECP and DK methods provide similar ROHF CBS limits; the

TABLE IV. Focal-point analysis of the classical barrier height ( $V_{SP}$ , cm<sup>-1</sup>) of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction based on all-electron effective core potential (ECP) as well as all-electron Douglas–Kroll (DK) computations.<sup>a</sup>

V SP[ROHF]	δ[RMP2]	δ[UCCSD]	$\delta$ [UCCSD(T)]	$V_{\rm SP}[\rm UCCSD(T)]$
9365	-3308	+502	-559	6000
9642	-3508	+750	-665	6219
9647	-3612	+780	-684	6130
9653	-3625	+787	-693	6122
9654	-3638	+794	-702	6108
V <sub>SP</sub> [ROHF]	$\delta$ [RMP2]	δ[UCCSD]	$\delta$ [UCCSD(T)]	$V_{SP}[UCCSD(T)]$
9313	-3404	+528	-557	5880
9648	-3660	+763	-672	6079
9654	-3666	+794	-687	6095
9660	-3682	+802	-696	6084
9661	-3700	+811	-704	6068
	9365 9642 9647 9653 9654 <u>V<sub>SP</sub>[ROHF]</u> 9313 9648 9654 9660 9661	9365 $-3308$ 9642 $-3508$ 9647 $-3612$ 9653 $-3625$ 9654 $-3638$ $V_{SP}[ROHF]$ $\delta[RMP2]$ 9313 $-3404$ 9648 $-3666$ 9654 $-3666$ 9654 $-3666$ 9660 $-3682$ 9661 $-3700$	9365 $-3308$ $+502$ 9642 $-3508$ $+750$ 9647 $-3612$ $+780$ 9653 $-3625$ $+787$ 9654 $-3638$ $+794$ $V_{SP}[ROHF]$ $\delta[RMP2]$ $\delta[UCCSD]$ 9313 $-3404$ $+528$ 9648 $-3660$ $+763$ 9654 $-3666$ $+794$ 9660 $-3682$ $+802$ 9661 $-3700$ $+811$	9365-3308+502-5599642-3508+750-6659647-3612+780-6849653-3625+787-6939654-3638+794-702 $V_{SP}[ROHF]$ $\delta[RMP2]$ $\delta[UCCSD]$ $\delta[UCCSD(T)]$ 9313-3404+528-5579648-3666+794-6879654-3666+794-6879660-3682+802-6969661-3700+811-704

<sup>a</sup>The ECP and DK results correspond to the structures optimized at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP and AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK levels of theory, respectively. The symbol  $\delta$  denotes the increments in  $V_{SP}$  with respect to the preceding level of theory.

<sup>b</sup>The complete basis set (CBS) ROHF energy and the RMP2, UCCSD, and UCCSD(T) electron correlation energies were calculated using two-parameter extrapolation formulae given in Eqs. (1) and (2), respectively. Only the best two energies were included in the extrapolations.

<sup>c</sup>Average value of the ECP and DK results.

 $^{d}$ Correlation energy increments obtained from FC-ECP UHF-UCCSD(T)  $\rightarrow$  UHF-UCCSDT  $\rightarrow$  UHF-UCCSDT(Q) computations with the aug-cc-pVDZ-PP basis set at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP geometries.

<sup>e</sup>Spin-orbit correction obtained from the experimental Br atom splitting ( $\varepsilon = 3685 \text{ cm}^{-1}$ ), as  $\varepsilon/3 = 1228 \text{ cm}^{-1}$ .

DK value is higher by only 7 cm<sup>-1</sup>. The  $\delta$ [RMP2] correlation energy effect on  $V_{SP}$  is huge; the ECP and DK CBS limits are -3638 and -3700 cm<sup>-1</sup>, respectively. The  $\delta$ [UCCSD] and  $\delta$ [UCCSD(T)] increments have similar magnitude and opposite sign, i.e., +794/+811 and -702/-704 cm<sup>-1</sup> with ECP/DK, respectively. The  $\delta$ [UCCSDT] and  $\delta$ [UCCSDT(Q)] increments, -47 and -37 cm<sup>-1</sup>, respectively, are much smaller, but still significant. Thus, RMP2 gives a fortuitously good estimate for  $V_{SP}$  due to error cancelations, UCCSD seriously overestimates  $V_{SP}$ , and the post-UCCSD(T) correlation effect lowers  $V_{SP}$  by about 84 cm<sup>-1</sup>. The neglected correlation effects beyond UCCSDT(Q) are expected to be less than  $10 \text{ cm}^{-1}$ . Considering the basis set effects, the DZ, TZ, QZ, and 5Z ECP/DK results differ from the corresponding CBS limits (6108/6068 cm<sup>-1</sup>) by 108/188, 111/11, 22/27, and  $14/16 \text{ cm}^{-1}$ , respectively. Our final benchmark non-SO  $V_{\rm SP}$  result is obtained by summing the average value of the ECP and DK UCCSD(T)/CBS results (6088  $cm^{-1}$ ) and the post-UCCSD(T) correlation effect ( $-84 \text{ cm}^{-1}$ ), resulting in a non-SO  $V_{SP}$  of 6004  $\pm$  50 cm<sup>-1</sup>. The uncertainty is estimated considering the two major sources that are the difference between the ECP and DK results and the uncertainty of the post-UCCSD(T) correlation effect. Using the experimental SO correction of +1228 cm<sup>-1</sup>, we arrive to the benchmark SO  $V_{SP}$ of  $7232 \pm 50$  cm<sup>-1</sup>. The harmonic ZPE correction for the barrier height is substantial  $(-1469 \text{ cm}^{-1})$ ; thus, the adiabaticvibrational-ground-state barrier height is 5763  $\pm$  120 cm<sup>-1</sup> (the larger uncertainty is mainly due to the neglected effect of vibrational anharmonicity).

Table V shows the FPA analysis for the dissociation energy of the CH<sub>3</sub>-HBr complex. The ROHF method gives unphysical negative  $D_e$  values of -309/-321 cm<sup>-1</sup> at the ECP/DK CBS limits, demonstrating that electron correlation plays a major role in stabilizing molecular complexes. Indeed, the  $\delta$ [RMP2] correlation increment in  $D_e$  is a large positive value of 1193/1217 cm<sup>-1</sup>, again at the ECP/DK CBS limits. RMP2 over-stabilizes, because  $\delta$ [UCCSD] is -285/  $-292 \text{ cm}^{-1}$ .  $\delta$ [UCCSD(T)] stabilizes by  $+181/+184 \text{ cm}^{-1}$ and  $\delta$ [UCCSDT] and  $\delta$ [UCCSDT(Q)] further increase the  $D_e$ by +7 and +8 cm<sup>-1</sup>, respectively. The ECP/DK UCCSD(T) computations with the DZ, TZ, QZ, and 5Z basis sets overestimate the CBS limit of  $D_e$  by 126/117, 60/86, 23/20, and 10/8 cm<sup>-1</sup>, respectively. As seen, the  $D_e$  value smoothly converges to the CBS limit and the uncertainty of the extrapolation is likely less than  $10 \text{ cm}^{-1}$ . The ECP and DK methods provide UCCSD(T)/CBS results close to each other, i.e., 780 and 788 cm<sup>-1</sup>, thus, the average value of 784 cm<sup>-1</sup> has a small uncertainty. Considering the post-UCCSD(T) correlation effect of  $+15 \text{ cm}^{-1}$  (see footnote d of Table V), we arrive to the benchmark  $D_{\rm e}$  of 799  $\pm$  10 cm<sup>-1</sup>. The harmonic ZPE correction is large (-480 cm<sup>-1</sup>); thus, the  $D_0$  value is only 319  $\pm$  $50 \text{ cm}^{-1}$ . Since the ZPE correction has significant uncertainty due to the harmonic approximation,  $D_0$  has larger uncertainty than  $D_{\rm e}$ , but we can still be confident that the CH<sub>3</sub>-HBr complex exists in its vibrational ground state.

The FPA results for the CH<sub>3</sub>–BrH complex are given in Table VI. Similar to CH<sub>3</sub>–HBr, the ROHF method also gives negative  $D_e$  for the CH<sub>3</sub>–BrH complex. The  $\delta$ [RMP2],  $\delta$ [UCCSD], and  $\delta$ [UCCSD(T)] increments in  $D_e$  are +582/+586, -119/-120, and +84/+84 cm<sup>-1</sup> at the ECP/DK CBS limits, respectively. The UCCSD(T) method provides very accurate  $D_{e}$ , since  $\delta$ [UCCSDT] and  $\delta$ [UCCSDT(Q)] are only +2 and +3 cm<sup>-1</sup>, respectively. The ECP and DK  $D_e$  values differ by only  $2 \text{ cm}^{-1}$ . The UCCSD(T) computations converge smoothly to the CBS limit as the basis size increases, since the DZ, TZ, QZ, and 5Z ECP/DK results overestimate  $D_{\rm e}$  by 80/94, 29/40, 17/18, and 8/8 cm<sup>-1</sup>, respectively. The best estimate for the  $D_e$  of CH<sub>3</sub>-BrH is 344  $\pm$  10 cm<sup>-1</sup>. The harmonic ZPE correction  $(-256 \text{ cm}^{-1})$  is very significant again, providing a  $D_0$  of only  $88 \pm 50$  cm<sup>-1</sup>. Note that the  $D_{\rm e}$  value has very high accuracy with small uncertainty; thus, the CH<sub>3</sub>-BrH minimum exists on the PES, which may

TABLE V. Focal-point analysis of the dissociation energy ( $D_e$ , cm<sup>-1</sup>) of the CH<sub>3</sub>–HBr complex based on all-electron effective core potential (ECP) as well as all-electron Douglas–Kroll (DK) computations.<sup>a</sup>

ECP	D <sub>e</sub> [ROHF]	δ[RMP2]	δ[UCCSD]	$\delta$ [UCCSD(T)]	D <sub>e</sub> [UCCSD(T)]
aug-cc-pwCVDZ-PP	-261	+1242	-230	+154	906
aug-cc-pwCVTZ-PP	-291	+1226	-270	+175	840
aug-cc-pwCVQZ-PP	-304	+1210	-282	+179	803
aug-cc-pwCV5Z-PP	-308	+1202	-284	+180	790
CBS <sup>b</sup>	-309	+1193	-285	+181	780
DK	$D_{\rm e}[{\rm ROHF}]$	δ[RMP2]	$\delta$ [UCCSD]	$\delta$ [UCCSD(T)]	$D_{e}[UCCSD(T)]$
aug-cc-pwCVDZ-DK	-256	+1248	-238	+152	905
aug-cc-pwCVTZ-DK	-304	+1273	-273	+178	874
aug-cc-pwCVQZ-DK	-315	+1226	-285	+181	808
aug-cc-pwCV5Z-DK	-320	+1222	-288	+182	796
CBS <sup>b</sup>	-321	+1217	-292	+184	788
$D_e(\text{final}) = D_e(\text{AE-UCCSD})$	T)/CBS) <sup>c</sup> + $\delta$ [UCCSDT] <sup>c</sup>	$d^{d} + \delta [UCCSDT(Q)]^{d} = 1$	784 + 7 + 8 = <b>799</b>		

<sup>a</sup>The ECP and DK results correspond to the structures optimized at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP and AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK levels of theory, respectively. The symbol  $\delta$  denotes the increments in  $D_e$  with respect to the preceding level of theory.

<sup>b</sup>The complete basis set (CBS) ROHF energy and the RMP2, UCCSD, and UCCSD(T) electron correlation energies were calculated using two-parameter extrapolation formulae given in Eqs. (1) and (2), respectively. Only the best two energies were included in the extrapolations.

<sup>c</sup>Average value of the ECP and DK results.

 $^{d}$ Correlation energy increments obtained from FC-ECP UHF-UCCSD(T)  $\rightarrow$  UHF-UCCSDT  $\rightarrow$  UHF-UCCSDT(Q) computations with the aug-cc-pVDZ-PP basis set at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP geometries.

TABLE VI.	Focal-point analysis of the dissociation energy (De, cm <sup>-</sup>	1) of the CH <sub>3</sub> –BrH	complex based o	on all-electron effect	tive core potenti	al (ECP)	as well
as all-electron	n Douglas-Kroll (DK) computations. <sup>a</sup>						

ECP D <sub>e</sub> [ROHF]		$\delta$ [RMP2]	δ[UCCSD]	$\delta$ [UCCSD(T)]	$D_{\rm e}[{\rm UCCSD}({\rm T})]$	
aug-cc-pwCVDZ-PP	-151	+589	-83	+65	420	
aug-cc-pwCVTZ-PP	-196	+598	-110	+77	369	
aug-cc-pwCVQZ-PP	-203	+597	-119	+82	357	
aug-cc-pwCV5Z-PP	-206	+590	-119	+83	348	
CBS <sup>b</sup>	-206	+582	-119	+84	340	
DK	D <sub>e</sub> [ROHF]	δ[RMP2]	$\delta$ [UCCSD]	$\delta$ [UCCSD(T)]	$D_{e}[UCCSD(T)]$	
aug-cc-pwCVDZ-DK	-140	+592	-85	+65	432	
aug-cc-pwCVTZ-DK	-204	+615	-111	+78	378	
aug-cc-pwCVQZ-DK	-208	+601	-120	+82	356	
aug-cc-pwCV5Z-DK	-212	+594	-120	+83	346	
CBS <sup>b</sup>	-212	+586	-120	+84	338	
$D_{\rm e}({\rm final}) = D_{\rm e}({\rm AE-UCCSD})$	$T)/CBS)^{c} + \delta[UCCSDT]^{c}$	$^{l} + \delta [UCCSDT(Q)]^{d} =$	339 + 2 + 3 = 344			

<sup>a</sup>The ECP and DK results correspond to the structures optimized at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP and AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK levels of theory, respectively. The symbol  $\delta$  denotes the increments in  $D_e$  with respect to the preceding level of theory.

<sup>b</sup>The complete basis set (CBS) ROHF energy and the RMP2, UCCSD, and UCCSD(T) electron correlation energies were calculated using two-parameter extrapolation formulae given in Eqs. (1) and (2), respectively. Only the best two energies were included in the extrapolations.

<sup>c</sup>Average value of the ECP and DK results.

 $^{d}$ Correlation energy increments obtained from FC-ECP UHF-UCCSD(T)  $\rightarrow$  UHF-UCCSDT  $\rightarrow$  UHF-UCCSDT(Q) computations with the aug-cc-pVDZ-PP basis set at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP geometries.

have an effect on the dynamics of the "negative-barrier" HBr + CH<sub>3</sub> reaction. Although the uncertainty of the ZPE due to the neglected anharmonic effects is significant, this well likely can support a vibrational ground state complex.

The FPA analysis of the enthalpy of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction is presented in Table VII. ROHF converges to its CBS limit rapidly, the 5Z and CBS results are the same within 1 cm<sup>-1</sup>; however, overestimates the endothermicity by about 9 %. The  $\delta$ [RMP2],  $\delta$ [UCCSD], and  $\delta$ [UCCSD(T)] increments are -519/-552, +157/+167, and -214/-214 cm<sup>-1</sup> at the ECP/DK CBS limits, respectively, whereas  $\delta$ [UCCSDT] and  $\delta$ [UCCSDT(Q)] are only -3 and  $-21 \text{ cm}^{-1}$ , respectively. The difference between the ECP and DK UCCSD(T)/CBS limits is 32 cm<sup>-1</sup>, which causes the largest source of the uncertainty of the final benchmark data. The ECP/DK UCCSD(T) with DZ basis underestimates the CBS limit by 53/171 cm<sup>-1</sup>, whereas TZ computations overestimate by 155/79 cm<sup>-1</sup>, and then the QZ and 5Z results converge monotonically as the deviations are 36/38 and 19/20 cm<sup>-1</sup>, in order. The final endothermicities, considering the average value (6653 cm<sup>-1</sup>) of the ECP (6669 cm<sup>-1</sup>) and DK (6637 cm<sup>-1</sup>) UCCSD(T)/CBS results, the post-UCCSD(T) correction ( $-24 \text{ cm}^{-1}$ ), and the SO effect ( $+1228 \text{ cm}^{-1}$ ), are 6629  $\pm$  50 and 7857

TABLE VII. Focal-point analysis of the vibrationless endoergicity ( $\Delta E_e, cm^{-1}$ ) of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction based on all-electron effective core potential (ECP) as well as all-electron Douglas–Kroll (DK) computations.<sup>a</sup>

ECP	$\Delta E_{\rm e}[{\rm ROHF}]$	$\delta$ [RMP2]	$\delta$ [UCCSD]	$\delta$ [UCCSD(T)]	$\Delta E_{\rm e}[\rm UCCSD(T)]$
aug-cc-pwCVDZ-PP	7061	-279	+4	-169	6616
aug-cc-pwCVTZ-PP	7259	-410	+174	-199	6824
aug-cc-pwCVQZ-PP	7244	-503	+169	-204	6705
aug-cc-pwCV5Z-PP	7244	-511	+163	-209	6688
CBS <sup>b</sup>	7245	-519	+157	-214	6669
DK	$\Delta E_{\rm e}[{\rm ROHF}]$	$\delta$ [RMP2]	$\delta$ [UCCSD]	$\delta$ [UCCSD(T)]	$\Delta E_{\rm e}[\rm UCCSD(T)]$
aug-cc-pwCVDZ-DK	7004	-386	+19	-171	6466
aug-cc-pwCVTZ-DK	7246	-512	+183	-202	6716
aug-cc-pwCVQZ-DK	7234	-534	+179	-205	6675
aug-cc-pwCV5Z-DK	7236	-543	+173	-209	6657
CBS <sup>b</sup>	7236	-552	+167	-214	6637

<sup>a</sup>The ECP and DK results correspond to the structures optimized at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP and AE-DK-UCCSD(T)/aug-cc-pwCVTZ-DK levels of theory, respectively. The symbol  $\delta$  denotes the increments in  $\Delta E_e$  with respect to the preceding level of theory.

<sup>b</sup>The complete basis set (CBS) ROHF energy and the RMP2, UCCSD, and UCCSD(T) electron correlation energies were calculated using two-parameter extrapolation formulae given in Eqs. (1) and (2), respectively. Only the best two energies were included in the extrapolations.

<sup>c</sup>Average value of the ECP and DK results.

 $^{d}$ Correlation energy increments obtained from FC-ECP UHF-UCCSD(T)  $\rightarrow$  UHF-UCCSDT  $\rightarrow$  UHF-UCCSDT(Q) computations with the aug-cc-pVTZ-PP basis set at the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP geometries.

<sup>e</sup>Spin-orbit correction obtained from the experimental Br atom splitting ( $\varepsilon = 3685 \text{ cm}^{-1}$ ), as  $\varepsilon/3 = 1228 \text{ cm}^{-1}$ .

TABLE VIII. Summary of the focal-point analysis results (in cm<sup>-1</sup>) showing the complete basis set (CBS) results at ROHF and all-electron RMP2, UCCSD, and UCCSD(T) levels as well as the effects of the post-CCSD(T) electron correlation (T(Q)), the spin-orbit (SO) couplings, and zero-point vibrational energy (ZPE) for the barrier height and enthalpy of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction as well as for the dissociation energies of CH<sub>3</sub>–HBr and CH<sub>3</sub>–BrH.

	Barrier height	Dissociatio	Reaction enthalpy	
	(CH <sub>3</sub> –H–Br) <sub>SP</sub>	CH <sub>3</sub> –HBr	CH <sub>3</sub> –BrH	$Br + CH_4 \rightarrow HBr + CH_3$
ROHF/CBS <sup>a</sup>	9654,9661	-309,-321	-206,-212	7245,7236
AE-RMP2/CBS <sup>a</sup>	6016,5961	884,897	376,373	6725,6684
AE-UCCSD/CBS <sup>a</sup>	6810,6772	598,604	256,254	6882,6851
AE-UCCSD(T)/CBS <sup>a</sup>	6108,6068	780,788	340,338	6669,6637
$\Delta T(Q)^{b}$	-84	+15	+5	-24
$\Delta SO^{c}$	+1228	+0	+0	+1228
Final classical <sup>d</sup>	7232	799	344	7857
$\Delta ZPE^{e}$	-1469	-480	-256	-1986(-1928)
Final + $\Delta ZPE$	5763	319	88	5871(5929)

<sup>a</sup>The two slightly different CBS results correspond to ECP and DK computations as ECP, DK. See Tables IV–VII and their footnotes.

<sup>b</sup>Post-CCSD(T) correlation corrections obtained as the difference between FC-ECP-UCCSD(T) and FC-ECP-UCCSDT(Q) energies computed with the aug-cc-pVDZ-PP, aug-ccpVDZ-PP, and aug-cc-pVTZ-PP basis sets for the barrier height, dissociation energies, and reaction enthalpy, respectively.

<sup>c</sup>Spin-orbit corrections obtained from the experimental Br atom splitting ( $\varepsilon = 3685 \text{ cm}^{-1}$ ), as  $\varepsilon/3 = 1228 \text{ cm}^{-1}$ .

<sup>d</sup>Average value of the ECP and DK AE-UCCSD(T)/CBS results +  $\Delta T(Q) + \Delta SO$ .

eHarmonic zero-point vibrational energy (ZPE) corrections obtained at the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP level of theory. For the reaction enthalpy the AE-ECP-UCCSD(T)/aug-cc-pVTZ-PP harmonic and, in parenthesis, the variationally computed anharmonic ZPE corrections are given.

 $\pm$  50 cm<sup>-1</sup> without and with SO correction, respectively. Considering harmonic and anharmonic ZPE corrections of -1986 and -1928 cm<sup>-1</sup>, respectively, the 0 K reaction enthalpies, including SO corrections, are 5871 and 5929  $\pm$  80 cm<sup>-1</sup>. For this thermochemical quantity we can compare the present computed result of 5929  $\pm$  80 cm<sup>-1</sup> to the reaction enthalpy of 5873  $\pm$  39 cm<sup>-1</sup> obtained from the 0 K enthalpies of formation of the species Br (9858  $\pm$  10 cm<sup>-1</sup>), CH<sub>4</sub> (-5570  $\pm$  25 cm<sup>-1</sup>), HBr (-2377  $\pm$  13 cm<sup>-1</sup>), and CH<sub>3</sub> (12539  $\pm$  25 cm<sup>-1</sup>) taken from the NIST database. We can also compare the computed reaction enthalpy to the barrier height. Without ZPE, the barrier height of  $7232 \pm 50 \text{ cm}^{-1}$  is clearly below the HBr + CH<sub>3</sub> asymptote of 7857  $\pm$  50 cm<sup>-1</sup>; thus, the classical barrier height of the HBr + CH<sub>3</sub> reaction is negative. When ZPE correction is included the adiabatic barrier height of 5763  $\pm$  120 cm<sup>-1</sup> is still below the reaction enthalpy of  $5871 \pm 80 \text{ cm}^{-1}$  indicating a slightly negative adiabatic barrier for the HBr + CH<sub>3</sub> reaction, though the uncertainty of this prediction is large. Note that here we use the harmonic ZPE correction for the reaction enthalpy in order to make a consistent comparison with the adiabatic barrier height.

Summary of the FPA analysis for the thermochemical data of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction is given in Table VIII. It is generally true that the ROHF method gives unreasonable results, especially for the barrier height and the binding energies of the vdW complexes. Even if ECP and DK, the two different approaches employed to account for scalar relativistic effects, gave similar results, at the accuracy of the present study the difference between the ECP and DK values was one of the major sources of the uncertainty for the classical barrier height and reaction enthalpy. The ZPE corrections were found substantial in all cases. The schematic of the PES of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction showing the structures of the stationary points and the corresponding new benchmark energies (excluding ZPE) is presented in

Fig. 2. Comparing the Br + CH<sub>4</sub> PES to the PES of the Cl + CH<sub>4</sub> reaction, beside many similarities (late-barrier and complexes in the entrance and product channels), we can observe major differences such as the SO shift from <sup>2</sup>P to <sup>2</sup>P<sub>3/2</sub> is about 4 times larger for Br than Cl, the classical barrier height and endothermicity are about 3 and 4 times higher for the Br + CH<sub>4</sub> reaction, respectively, and the classical barrier height is negative for the HBr + CH<sub>3</sub> reaction, whereas positive for HCl + CH<sub>3</sub>.<sup>15,16</sup>

#### III. AB INITIO NON-SPIN-ORBIT AND SPIN-ORBIT GROUND-STATE POTENTIAL ENERGY SURFACES

The two key steps of the present PES development are (1) the computation of a large number of *ab initio* energy points and (2) the representation of the PES by an analytical function. First, we describe below how we test the performance of different *ab initio* levels of theory for the title reaction and we propose an efficient composite approach which gives high-quality energy points with affordable computational cost. Second, we describe the details of the fit using the permutationally invariant polynomial approach.<sup>12, 13</sup> Finally, we compare the properties of the new non-SO and SO ground-state full-dimensional PESs to the best *ab initio* predictions.

#### A. The ab initio data

Our goal is to compute more than 10 000 accurate *ab initio* energy points within affordable computational time. We aim to obtain chemical accuracy (<1 kcal/mol) or even better; for example, an accuracy better than 0.5 kcal/mol (175 cm<sup>-1</sup>). To achieve this goal we have to consider the performance of different *ab initio* methods and basis sets. Furthermore, since the title reaction involves a heavy atom (Br), one has to pay special attention to core-electron correlation, scalar relativistic, and spin-orbit effects.



FIG. 2. Schematics of the non-SO and SO PESs of the Br +  $CH_4 \rightarrow HBr + CH_3$  reaction showing the accurate electronic energies and the corresponding PES values relative to  $Br(^2P_{3/2}) + CH_4(eq)$ . The accurate benchmark data (upper red numbers) are all-electron relativistic CCSDT(Q)/complete-basis-set quality results obtained from the present focal-point analysis.

We have selected 15 configurations representing different regions of the PES and covering energies up to 21 000 cm<sup>-1</sup> relative to Br + CH<sub>4</sub>(eq). For each configuration we have performed FC-ECP-UMP2 and FC-ECP-UCCSD(T) computations with the aug-cc-pV*n*Z-PP [n = D, T, Q] basis sets as well as AE-ECP-UMP2 and AE-ECP-UCCSD(T) computations with the aug-cc-pwCV*n*Z-PP [n = D, T, Q] basis sets. As reference results we use the highly accurate AE-ECP-UCCSD(T)/aug-cc-pwCVQZ-PP data and we consider the root-mean-square (RMS) errors of the different levels of theory relative to these reference energies. Note that the also highly accurate AE-DK-UCCSD(T)/aug-cc-pwCVQZ-DK energies agree with the above ECP reference data with a RMS of only 36 cm<sup>-1</sup> (0.1 kcal/mol). Figure 3 shows the RMS errors of the above described *ab initio* methods/bases. As seen, neither frozen-core nor all-electron UMP2 calculations provide chemical accuracy. Furthermore, if we use the usual frozen-core approach, even the UCCSD(T) method is insufficient to achieve our target accuracy, since the FC-ECP-UCCSD(T) RMS errors are 1249, 463, and 319 cm<sup>-1</sup> for *n* 



FIG. 3. Accuracy of the different frozen-core and all-electron *ab initio* correlation methods and bases based on computations at 15 representative configurations along the reaction coordinate of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction. The 15 energies are relative to Br + CH<sub>4</sub>(eq) and span a range from 0 to 21 000 cm<sup>-1</sup>. The RMS errors are relative to high-quality reference results obtained at the AE-ECP-UCCSD(T)/aug-cc-pwCVQZ-PP level of theory. All the computations employed ECP for Br and the corresponding aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP [n = D, T, Q] basis sets for frozen-core and all-electron computations, respectively. The all-electron composite energy is defined as *E*[AE-ECP-UCCSD(T)/aug-cc-pwCVDZ-PP] + *E*[AE-ECP-UMP2/aug-cc-pwCVTZ-PP] – *E*[AE-ECP-UMP2/aug-cc-pwCVDZ-PP].

= D, T, and Q, respectively. This indicates that we need to consider the correlation of the core electrons. Indeed, the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP level of theory outperforms even the also very expensive FC-ECP-UCCSD(T)/aug-cc-pVQZ-PP level and provides really accurate results with a RMS of only 109 cm<sup>-1</sup>. However, due to the many core electrons in the Br + CH<sub>4</sub> system, the AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP level of theory is too time consuming to compute more than 10 000 energies, especially without symmetry. Therefore, we use a composite approach, where the energies are defined as

$$E[AE-ECP-UCCSD(T)/aug-cc-pwCVDZ-PP]$$
  
+  $E[AE-ECP-UMP2/aug-cc-pwCVTZ-PP]$   
-  $E[AE-ECP-UMP2/aug-cc-pwCVDZ-PP].$  (3)

As also shown in Fig. 3, this composite method provides high-quality results with a RMS of only 129  $cm^{-1}$  relative to AE-ECP-UCCSD(T)/aug-cc-pwCVQZ-PP. This RMS is very similar to that of AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP but the cost of the composite energies is significantly less (by a factor of about 15, of course, depending on the ab *initio* program employed). It is important to emphasize that this composite method significantly outperforms the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP and FC-ECP-UCCSD(T)/augcc-pVQZ-PP "high" levels (see Fig. 3). The performance of this composite method is further analyzed in Fig. 4, where we show the individual errors of the three components of the composite energy at 15 different geometries. It is seen that each level of theory given in Eq. (3) provides significant deviations, sometimes larger than  $500-1000 \text{ cm}^{-1}$  with varying signs, from the accurate reference results, whereas the composite energies are always close to the high-quality reference data.



FIG. 4. Accuracy of the composite method based on computations at 15 representative configurations for the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction. E = 0 corresponds to the Br + CH<sub>4</sub>(eq) asymptote and the errors are relative to high-quality reference results obtained at the AE-ECP-UCCSD(T)/aug-cc-pwCVQZ-PP level of theory. All the computations used ECP for Br and all the electrons were correlated. The composite energy is defined as E[AE-ECP-UCCSD(T)/aug-cc-pwCVDZ-PP] + E[AE-ECP-UMP2/aug-cc-pwCVDZ-PP].



FIG. 5. Spin-orbit correction curves for the entrance channel of the Br + CH<sub>4</sub> reaction as a function of the C–Br distance along the  $C_3$  axis keeping CH<sub>4</sub> at equilibrium with H<sub>3</sub>CH–Br and HCH<sub>3</sub>–Br orientations. The SO correction is defined as the difference between the SO and non-SO ground-state electronic energies. The curves were obtained by the AE-ECP-MRCI+Q/aug-cc-pwCVDZ-PP level of theory and the PES values, i.e., differences between the SO and non-SO PESs, are also shown for comparison.

The SO effects are considered as an additive correction to the non-SO composite energy defined in Eq. (3). We compute the SO corrections as  $E_{SO} - E_{non-SO}$ , where  $E_{SO}$  and  $E_{\text{non-SO}}$  are the SO ground-state and non-SO ground-state electronic energies, respectively, obtained at the AE-ECP-MRCI+Q/aug-cc-pwCVDZ-PP level of theory. The SO corrections as a function of the CH<sub>4</sub>-Br inter-fragment separation are shown in Fig. 5. As seen, the nearly constant value at distances larger than 4 Å decreases as Br approaches CH<sub>4</sub> and tends to vanish at C-Br distances less than about 2 Å. The SO effect depends on the relative orientation of the reactants; the HCH<sub>3</sub>-Br configurations usually give substantially larger absolute corrections than the H<sub>3</sub>CH-Br orientations at the same C-Br distances. For example, at a C-Br distance of 3.0 Å, the SO corrections are -457 and -860 cm<sup>-1</sup> for H<sub>3</sub>CH-Br and HCH<sub>3</sub>-Br, respectively. Since the SO correction is only significant in the entrance channel of the  $Br + CH_4$  reaction, we have selected structures from the total set of configurations based on the following geometrical conditions:

$$r(C-Br) > 2.0 \text{ Å and } \min[r(H-Br)] > 1.5 \text{ Å and}$$
  
 $\max[r(C-H)] < 1.4 \text{ Å.}$  (4)

Equation (4) resulted in 3127 entrance-channel configurations (excluding the 2000 Br + CH<sub>4</sub> fragment data, where a constant SO correction is applied), where the SO corrections have been computed and the  $E_{SO} - E_{non-SO}$  energy differences have been added to the non-SO composite energies.

#### B. Fitting the ab initio energies

We have used the above defined composite method to compute a total number of 21 574 *ab initio* energy points. The dataset includes 14 743 BrCH<sub>4</sub> configurations in the complex region and 2000, 1922, 1909, and 1000 energy points for the fragment channels Br + CH<sub>4</sub>, HBr + CH<sub>3</sub>, H<sub>2</sub> + CH<sub>2</sub>Br, and H + CH<sub>3</sub>Br, respectively. There are 3687/3483, 4015/3897, 6776/6972, and 7096/7222 non-SO/SO energy points in

TABLE IX. Properties of the stationary points of the potential energy surface (PES).

	(CH	(CH <sub>3</sub> -H <sub>b</sub> -Br) <sub>SP</sub>			CH <sub>3</sub> -H <sub>b</sub> Br			C	H <sub>3</sub> –BrH <sub>b</sub>		
	PES <sup>a</sup>	aVTZ <sup>b</sup>	Acc. <sup>c</sup>		PES <sup>a</sup>	aVTZ <sup>b</sup>	Acc. <sup>c</sup>		PES <sup>a</sup>	aVTZ <sup>b</sup>	Acc. <sup>c</sup>
Structures (	Å and degree)										
r(CH)	1.081/1.081	1.082	1.081	r(CH)	1.080/1.080	1.081	1.079	r(CH)	1.081/1.081	1.080	1.078
r(CH <sub>b</sub> )	1.700/1.710	1.687	1.674	r(CH <sub>b</sub> )	2.186/2.210	2.183	2.184	r(CBr)	3.339/3.350	3.456	3.440
r(H <sub>b</sub> Br)	1.487/1.484	1.491	1.486	r(H <sub>b</sub> Br)	1.422/1.421	1.433	1.426	r(BrH <sub>b</sub> )	1.413/1.413	1.421	1.415
$\alpha(\text{HCH}_b)$	97.1/96.9	97.4	97.4	$\alpha(\text{HCH}_{b})$	92.5/92.5	93.0	93.0	$\alpha$ (HCBr)	90.3/90.3	90.4	90.4
Energies (cr	$m^{-1}$ ) relative to $h$	$Br + CH_4(ea$	<i>q</i> )								
Non-SO	6039	6402	6004	Non-SO	5762	6193	5830	Non-SO	6226	6664	6285
SO	7285	7630 <sup>d</sup>	7232 <sup>d</sup>	SO	7001	7421 <sup>d</sup>	7058 <sup>d</sup>	SO	7468	7892 <sup>d</sup>	7513 <sup>d</sup>
Energies (cr	$m^{-1}$ ) relative to $h$	HBr(eq) + C	$CH_3(eq)$								
Non-SO	-598	-627	-625	Non-SO	-875	-837	-799	Non-SO	-411	-366	-344
SO	-583	-627	-625	SO	-867	-837	-799	SO	-399	-366	-344

<sup>a</sup>Results corresponding to the non-SO and SO PESs. The two PESs give slightly different structural parameters; both are presented as non-SO/SO.

<sup>b</sup>Results obtained by *ab initio* calculations at the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP level of theory.

<sup>c</sup>Accurate structures obtained at AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP level of theory. The highly accurate relative energies were obtained from the focal-point analysis as given in Table VIII.

<sup>d</sup>The SO energy shift is obtained from the experimental Br atom splitting ( $\varepsilon = 3685 \text{ cm}^{-1}$ ), as  $\varepsilon/3 = 1228 \text{ cm}^{-1}$ .

the energy intervals (0, 11000), (11000, 22000), (22000, 55 000), and > 55 000 cm<sup>-1</sup>, respectively. We have used the permutationally invariant polynomial approach<sup>12,13</sup> to fit the non-SO and SO-corrected energy points. The analytical PES is a polynomial expansion of a basis that is invariant under permutations of the identical atoms. To get favorable asymptotic behavior the permutationally invariant basis functions are expressed in Morse-like variables,  $y_{ij} = \exp(-r_{ij}/a)$ , where  $r_{ij}$  are the inter-atomic distances and a = 2 bohrs. We have done sixth-order weighted (an energy (E) relative to the global minimum has weight  $E_0/(E + E_0)$ , where  $E_0 = 11\,000 \text{ cm}^{-1}$ ) linear least-squares fits of the non-SO and the SO energies, which result in 3262 coefficients for each PES. For the non-SO/SO PESs the RMS fitting errors are 64/63, 132/140, and 358/347 cm<sup>-1</sup> for energy ranges 0–11000, 11000–22000, and  $22\,000-55\,000$  cm<sup>-1</sup>, respectively. Note that the RMS errors up to  $22\,000$  cm<sup>-1</sup>, the energy range most important for chemical applications, are below the target accuracy of the present study and the accuracy of the fits is similar to the accuracy of the composite *ab initio* energy points.

#### C. The properties of the non-SO and SO potential energy surfaces

We have carried out geometry optimizations and harmonic frequency computations on the new PESs in order to compare the relative energies, structures, and frequencies of the stationary points to the new benchmark data described in Sec. II.

In Fig. 1 one-dimensional cuts for the entrance channel as a function of the Br–CH<sub>4</sub>(eq) distance are shown. The PESs give a splitting of 1240 cm<sup>-1</sup> between the Br(<sup>2</sup>P) and Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub> asymptotes, in excellent agreement with experiment (1228 cm<sup>-1</sup>). As also shown in Fig. 1, both the non-SO and SO PESs describe the shallow vdW wells showing that the HCH<sub>3</sub>–Br orientation is the deeper minimum, in good agreement with the direct *ab initio* AE-ECP-MRCI+Q/aug-cc-pwCVDZ-PP curves. In Fig. 5 the SO corrections, i.e., the differences between the SO and non-SO ground-state electronic energies, are shown obtained from direct *ab initio* computations and from the PESs. It is seen that the PES values reproduce the correct distance and orientation dependence of the SO corrections, in good agreement with the direct *ab initio* data.

In Tables IX and X the structures and energetics of the saddle point,  $CH_3$ -HBr and  $CH_3$ -BrH complexes, and reactants and products are given. It is important to note that the SO correction has no effect on these structures; however, since the fits are global, the significant SO corrections in the entrance channel can result in slight differences between the product regions of the non-SO and SO PESs. As seen in Table IX, these differences are negligible and many structural parameters agree within 0.001 Å on the two PESs. Considering ( $CH_3$ - $H_b$ -Br)<sub>SP</sub>, the CH,  $CH_b$ , and  $H_b$ Br distances on the non-SO/SO PESs are 1.081/1.081,

TABLE X. Properties of the potential energy surface (PES) for the reactants and products.

		$Br + CH_4$			]	HBr + CH	3
	PES <sup>a</sup>	aVTZ <sup>b</sup>	Acc. <sup>c</sup>		PES <sup>a</sup>	aVTZ <sup>b</sup>	Acc. <sup>c</sup>
Structures	s (Å)						
r(CH)	1.089	1.090	1.087	r(CH)	1.078	1.080	1.076
				r(HBr)	1.412	1.420	1.413
Relative e	nergies (	$cm^{-1}$ )					
Non-SO	0	0	0	Non-SO	6637	7029	6629
SO	0	0	0	SO	7867	8257 <sup>d</sup>	7857 <mark>d</mark>

<sup>a</sup>Results corresponding to the non-SO and SO PESs. The two PESs give the same structural parameters within 0.001 Å.

<sup>&</sup>lt;sup>b</sup>Results obtained by *ab initio* calculations at the FC-UCCSD(T)/aug-cc-pVTZ level of theory. For Br ECP and the corresponding aug-cc-pVTZ-PP basis set were employed. <sup>c</sup>Accurate structures obtained at AE-UCCSD(T)/aug-cc-pwCVOZ level of theory. For

For a contract structures obtained at AE-UCCSD(1)/aug-cc-pwCVQZ level of theory. For Br ECP and the corresponding aug-cc-pwCVQZ-PP basis set were employed. The highly accurate relative energies were obtained from the focal-point analysis as given in Table VIII.

<sup>&</sup>lt;sup>d</sup>The SO energy shift is obtained from the experimental Br atom splitting ( $\varepsilon = 3685 \text{ cm}^{-1}$ ), as  $\varepsilon/3 = 1228 \text{ cm}^{-1}$ .

TABLE XI. Harmonic vibrational frequencies (in cm<sup>-1</sup>) for (CH<sub>3</sub>-H-Br)<sub>SP</sub>, CH<sub>3</sub>-HBr, and CH<sub>3</sub>-BrH.

	(CH <sub>3</sub> -H-Br) <sub>SP</sub>				CH <sub>3</sub> –HBr					CH <sub>3</sub> –BrH		
	PES <sup>a</sup>	aVDZ <sup>b</sup>	aVTZ <sup>b</sup>		PES <sup>a</sup>	aVDZ <sup>b</sup>	aVTZ <sup>b</sup>		PES <sup>a</sup>	aVDZ <sup>b</sup>	aVTZ <sup>b</sup>	
ZPE	8390	8267	8364	ZPE	8414	8262	8321	ZPE	8071	8072	8097	
$\omega(a_1)$	303 <i>i</i>	272 <i>i</i>	261 <i>i</i>	$\omega(a_1)$	98	79	82	$\omega(a_1)$	72	67	57	
$\omega(e)$	272	280	295	$\omega(e)$	173	141	156	$\omega(e)$	51	76	81	
$\omega(e)$	709	627	657	$\omega(e)$	370	307	338	$\omega(e)$	121	151	155	
$\omega(a_1)$	707	745	764	$\omega(a_1)$	693	590	602	$\omega(a_1)$	530	511	503	
$\omega(e)$	1446	1404	1427	$\omega(e)$	1403	1404	1419	$\omega(e)$	1424	1405	1418	
$\omega(a_1)$	1507	1562	1579	$\omega_{\rm HBr}(a_1)$	2478	2498	2459	$\omega_{\rm HBr}(a_1)$	2654	2630	2631	
$\omega_{\rm CH}(a_1)$	3105	3079	3094	$\omega_{\rm CH}(a_1)$	3100	3091	3104	$\omega_{\rm CH}(a_1)$	3079	3098	3110	
$\omega_{\rm CH}(e)$	3304	3262	3267	$\omega_{\rm CH}(e)$	3283	3281	3285	$\omega_{\rm CH}(e)$	3307	3287	3291	

<sup>a</sup>Harmonic frequencies corresponding to the SO PES. The non-SO PES gives similar frequencies (the largest deviations are 16, 23, and 25 cm<sup>-1</sup> for (CH<sub>3</sub>–H–Br)<sub>SP</sub>, CH<sub>3</sub>–HBr, and CH<sub>3</sub>–BrH, respectively).

<sup>b</sup>aVDZ and aVTZ denote *ab initio* results obtained at the FC-ECP-UCCSD(T)/aug-cc-pVDZ-PP and FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP levels of theory, respectively.

1.700/1.710, and 1.487/1.484 Å, in excellent agreement with the benchmark AE-ECP-UCCSD(T)/aug-cc-pwCVTZ-PP data of 1.081, 1.674, and 1.486 Å, respectively. For the CH and H<sub>b</sub>Br distances the PES gives better results than the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP data of 1.082 and 1.491 Å. Similar good agreement is seen for the PES and benchmark structures of the CH<sub>3</sub>-HBr and CH<sub>3</sub>-BrH complexes as also shown in Table IX. For example, the non-SO/SO PES CH, CH<sub>b</sub>, and H<sub>b</sub>Br distance data of the important CH<sub>3</sub>-H<sub>b</sub>Br complex are 1.080/1.080, 2.186/2.210, and 1.422/1.421 Å, respectively, again in good agreement with the corresponding benchmark results of 1.079, 2.184, and 1.426 Å. For CH<sub>4</sub>, HBr, and CH<sub>3</sub> the PES values agree with the AE-UCCSD(T)/aug-cc-pwCVQZ benchmark bond lengths within 0.002, 0.001, and 0.002 Å, respectively, whereas the FC-UCCSD(T)/aug-cc-pVTZ results deviate from the benchmarks by 0.003, 0.007, and 0.004 Å, respectively.

Comparison of the relative energies on the PESs with the benchmark data is shown in Fig. 2 as well as in Tables IX and X. The classical barrier heights on the non-SO and SO PESs are 6039 and 7285 cm<sup>-1</sup>, respectively, in excellent agreement with the corresponding benchmark FPA results of  $6004 \pm 50$ and  $7232 \pm 50$  cm<sup>-1</sup>. The PES is significantly more accurate than FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP, since this ab ini*tio* level gives classical barriers of 6402 and 7630  $\text{cm}^{-1}$  relative to  $Br(^{2}P)$  and  $Br(^{2}P_{3/2}) + CH_{4}$ , respectively, overestimating the barriers by roughly 1.1 kcal/mol, whereas the PESs are accurate within 0.16 kcal/mol. The depths of the CH<sub>3</sub>-HBr and  $CH_3$ –BrH minima relative to  $HBr(eq) + CH_3(eq)$  are 875/867 and 411/399 cm<sup>-1</sup> on the non-SO/SO PESs, respectively, whereas the corresponding benchmark De values are  $799 \pm 10$  and  $344 \pm 10$  cm<sup>-1</sup>. For the reaction endothermicity (excluding ZPE) the non-SO and SO PESs provide 6637 and 7867 cm<sup>-1</sup>, respectively, in fortuitously excellent agreement with the corresponding benchmark data of  $6629 \pm 50$ and 7857  $\pm$  50 cm<sup>-1</sup>, whereas FC-UCCSD(T)/aug-cc-pVTZ overestimates the endothermicity by  $400 \text{ cm}^{-1}$ .

Harmonic vibrational frequencies for  $(CH_3-H-Br)_{SP}$ ,  $CH_3-HBr$ , and  $CH_3-BrH$  obtained from the PESs and at FC-ECP-UCCSD(T)/aug-cc-pVnZ-PP [n = D and T] are given in Table XI, whereas the frequencies of CH<sub>4</sub>, CH<sub>3</sub>,

and HBr are given in Table XII. For the reactant and products we also performed more accurate AE-UCCSD(T)/aug-cc-pwCVnZ [n = D and T] computations as also shown in Table XII. Similar to the structures, the SO coupling does not affect the frequencies, but the global fits can result in slightly different results. In the discussion below the frequencies corresponding to the SO PES are given. (CH<sub>3</sub>-H-Br)<sub>SP</sub> is a first-order saddle point on the PES with a low imaginary frequency of 303i cm<sup>-1</sup>, whereas the benchmark value is 261i cm<sup>-1</sup>. The 12 (counting the e modes twice) harmonic fundamental frequencies on the PES agree with the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP results with RMS deviations of 41, 32, and 23 cm<sup>-1</sup> for (CH<sub>3</sub>-H-Br)<sub>SP</sub>, CH<sub>3</sub>-HBr, and CH<sub>3</sub>-BrH, respectively. For CH<sub>4</sub>, CH<sub>3</sub>, and HBr the RMS differences between the PES FC-UCCSD(T)/aug-cc-pVTZ(AE-UCCSD(T)/aug-ccand pwCVTZ) wavenumbers are 3(8), 13(21), and 41(27) cm<sup>-1</sup>. In the case of the CH<sub>3</sub>-HBr complex the HBr stretching frequency is 2478 cm<sup>-1</sup> on the PES, substantially redshifted by 207 cm<sup>-1</sup> relative to the frequency of the HBr molecule. The PES gives an accurate prediction for this redshift, since the FC-ECP-UCCSD(T)/aug-cc-pVTZ-PP value is 185 cm<sup>-1</sup>. Since the CH<sub>3</sub>-BrH complex is more weakly bonded, the redshift of the HBr fundamental is an order of magnitude smaller than that of the CH<sub>3</sub>–HBr complex.

#### **IV. QUASICLASSICAL TRAJECTORY CALCULATIONS**

#### A. Computational details

#### 1. Initial conditions

We perform full-dimensional QCT calculations for the  $Br(^{2}P_{3/2}) + CH_{4}(v_{k} = 0, 1) \rightarrow HBr + CH_{3}$  [k = 1, 2, 3, 4] reactions using the new SO PES. To investigate the effect of the SO correction, QCT calculations are also performed on the non-SO PES for the  $Br(^{2}P) + CH_{4}(v = 0)$  reaction. The vibrational ground state is denoted as v = 0, whereas  $v_{4}, v_{2}, v_{1}$ , and  $v_{3}$  are the umbrella, bending, symmetric stretching, and asymmetric stretching modes of CH<sub>4</sub>, respectively. Standard normal-mode sampling<sup>54</sup> is employed to prepare the initial quasiclassical vibrational ground and mode-specific excited

TABLE XII. Harmonic vibrational frequencies (in cm<sup>-1</sup>) for CH<sub>4</sub>, CH<sub>3</sub>, and HBr.

	CH <sub>4</sub>					CH <sub>3</sub>				HBr		
	PES <sup>a</sup>	aVDZ <sup>b</sup>	aVTZ <sup>b</sup>		PES <sup>a</sup>	aVDZ <sup>b</sup>	aVTZ <sup>b</sup>		PES <sup>a</sup>	aVDZ <sup>b</sup>	aVTZ <sup>b</sup>	
ZPE	9827	9738	9833	ZPE	6489	6495	6518	ZPE	1343	1320	1322	
$\omega_4(t_2)$	1351	1319	1351	$\omega_2(a_2'')$	481	497	496	$\omega_1$	2685	2640	2644	
$\omega_2(e)$	1571	1535	1574	$\omega_4(e')$	1421	1406	1419					
$\omega_1(a_1)$	3020	3016	3028	$\omega_1(a_1)$	3096	3101	3114					
$\omega_3(t_2)$	3146	3144	3146	$\omega_3(e')$	3280	3290	3294					
	PES <sup>a</sup>	awCVDZ <sup>c</sup>	awCVTZ <sup>c</sup>		PES <sup>a</sup>	awCVDZ <sup>c</sup>	awCVTZ <sup>c</sup>		PES <sup>a</sup>	awCVDZ <sup>c</sup>	awCVTZ <sup>c</sup>	
ZPE	9827	9743	9858	ZPE	6489	6500	6543	ZPE	1343	1326	1329	
$\omega_4(t_2)$	1351	1321	1353	$\omega_2(a_2'')$	481	503	509	$\omega_1$	2685	2651	2658	
$\omega_2(e)$	1571	1538	1577	$\omega_4(e')$	1421	1408	1423					
$\omega_1(a_1)$	3020	3016	3036	$\omega_1(a_1)$	3096	3102	3123					
$\omega_3(t_2)$	3146	3144	3156	$\omega_3(e')$	3280	3289	3304					

<sup>a</sup>Harmonic frequencies corresponding to the SO PES. The non-SO PES gives basically the same frequencies (the largest deviations are 7, 3, and 2 cm<sup>-1</sup> for CH<sub>4</sub>, CH<sub>3</sub>, and HBr, respectively).

<sup>b</sup>aVDZ and aVTZ denote *ab initio* results obtained at the FC-UCCSD(T)/aug-cc-pVDZ and FC-UCCSD(T)/aug-cc-pVTZ levels of theory, respectively. For Br ECP and the corresponding aug-cc-pVDZ-PP/aug-cc-pVTZ-PP basis set were employed.

<sup>c</sup>awCVDZ and awCVTZ denote *ab initio* results obtained at the AE-UCCSD(T)/aug-cc-pwCVDZ and AE-UCCSD(T)/aug-cc-pwCVTZ levels of theory, respectively. For Br ECP and the corresponding aug-cc-pwCVDZ-PP/aug-cc-pwCVTZ-PP basis set were employed.

states. The initial distance between the center of mass of the reactants is  $\sqrt{x^2 + b^2}$ , where *b* is the impact parameter and *x* = 10 bohrs. The orientation of CH<sub>4</sub> is randomly sampled and *b* is scanned from 0 to 6 bohrs with a step size of 0.5 bohrs. We compute 25 000 trajectories at each *b*; thus, the total number of trajectories is 325 000 for each collision energy (*E*<sub>coll</sub>). QCT calculations are carried out at 6, 7, and 8 different collision energies in the ranges 6000–16 000, 4000–16 000, and 2000–16 000 cm<sup>-1</sup> for the ground-state, bending/umbrellaexcited, and stretching-excited reactions, respectively. Thus, we run a total of 13 650 000 trajectories usually finish within a few hundred fs.

#### 2. Final conditions

We compute integral and differential cross sections as well as reaction probabilities at several collision energies. The QCT analysis considers all the trajectories without ZPE constraint as well as various treatments of the usual ZPE issue of QCT method. We use the soft, hard, and CH<sub>3</sub> vibrational energy-based ZPE constraints as well as Gaussian binning (1GB).55-57 The soft ZPE constraint discards trajectories if  $E_{vib}(HBr) + E_{vib}(CH_3)$  is less than the sum ZPE(HBr) + ZPE(CH<sub>3</sub>), whereas the hard constraint discards trajectories if either  $E_{vib}$ (HBr) or  $E_{vib}$ (CH<sub>3</sub>) is less than the corresponding ZPE. We also consider a CH<sub>3</sub> vibrational energybased ZPE constraint, which is only applied to the polyatomic product. The Gaussian binning is done using the 1GB strategy<sup>55,56</sup> based on the quantized harmonic vibrational energy compared to the classical vibrational energy of the product evaluated exactly in the Cartesian space as described in detail in Ref. 57. The weight of a trajectory is obtained as the product of the weights of HBr(v) and CH<sub>3</sub>( $n_1n_2n_3n_4$ ). 1GB has the advantage that only one Gaussian weight is computed for a polyatomic product, i.e., CH<sub>3</sub> in the present case.

#### B. Mode-selectivity for the Br + CH<sub>4</sub> reaction

Reactant vibrational mode-specific integral cross sections for the Br( ${}^{2}P_{3/2}$ ) + CH<sub>4</sub>( $v_{k} = 0, 1$ ) [k = 1, 2, 3, 4] reactions as a function of collision energy are given in Figure 6. The cross sections of the ground-state reaction are very small, at least an order of magnitude less than those of the Cl + CH<sub>4</sub>(v = 0) reaction.<sup>16</sup> We have found that reactant vibrational excitations have a substantial effect on the reactivity. Considering all the trajectories without ZPE constraint or weighting, the umbrella and bending excitations similarly enhance the reactivity by a factor of 5–7 around  $E_{coll}$  $= 8000 \text{ cm}^{-1}$  and at a large  $E_{\text{coll}}$  of 16 000 cm<sup>-1</sup> the enhancement factor is still around 3. The stretching modes have even much more significant effects on the reactivity, since the enhancement factors are 40–50 ( $v_1 = 1$ ) and 20–30 ( $v_3 = 1$ ) at  $E_{\text{coll}} = 8000 \text{ cm}^{-1}$  and around 10 ( $v_1 = 1$ ) and 8 ( $v_3 = 1$ ) at  $E_{\text{coll}} = 16\,000 \text{ cm}^{-1}$ . In Fig. 6 the ZPE(soft), ZPE(hard), and ZPE(CH<sub>3</sub>) constrained as well as 1GB results are also shown. As seen, most of the trajectories violate product ZPE, since the ZPE constrained cross sections are an order of magnitude less than the non-constrained results. The magnitude of the 1GB results is similar to the all trajectory ones, but the normalization of Gaussian binning for bimolecular processes is problematic, because we cannot simply assign weights for non-reactive trajectories. In the present study we compute the 1GB reaction probabilities as a sum of the weights of the reactive trajectories divided by the total number of trajectories. The soft and CH<sub>3</sub>-based constraints give very similar results, this was also found for the  $Cl + CH_4$  reaction,<sup>16</sup> whereas the hard ZPE constraint provides about 3 times smaller cross sections. Nevertheless, there are many similarities between the non-constrained and various ZPE constrained results. The significant vibrational enhancement effects are seen in all the cases. The ZPE constrained results show that the excitation of the stretching modes has much larger enhancement effects than that of the bending/umbrella modes, in agreement with the non-constrained results. Note that when the ZPE



FIG. 6. Cross sections as a function of collision energy for the ground-state (v = 0), bending-excited ( $v_4$  and  $v_2$ ), and stretching-excited ( $v_1$  and  $v_3$ ) Br( ${}^{2}P_{3/2}$ ) + CH<sub>4</sub>( $v_k = 0, 1$ ) [k = 1, 2, 3, 4] reactions obtained by considering (a) all trajectories without ZPE constraint or weighting, (b) soft, (c) hard, and (d) CH<sub>3</sub>-based ZPE constraints, in which trajectories are discarded if (b) the sum of the product vibrational energies is less than the sum of their ZPEs, (c) either product has less vibrational energy than its ZPE. (e) Gaussian binning was also employed using the 1GB procedure as described in Ref. 57.

constraint is employed the  $v_1$  and  $v_3$  stretching effects become similar, whereas without ZPE constraint the  $v_1$  mode has a larger enhancement effect on the reactivity. Another notable difference between the constrained and non-constrained results is seen for the threshold energies, since the thresholds are significantly higher if the ZPE constraint or 1GB is applied. For the thresholds the ZPE constrained or 1GB results seem more realistic. On the other hand, the ZPE constraints, especially the hard constraint, may underestimate the cross sections. Further studies based on rigorous quantum dynamics would be necessary to validate the present QCT results. For the similar  $O(^{3}P) + CH_{4}$  reaction we found recently that the non-constrained QCT integral cross sections are in good agreement with the quantum results.<sup>20</sup>

The Polanyi rules predict that vibrational energy is more efficient than translational energy to activate a late-barrier reaction. In order to investigate the validity of these rules for the late-barrier Br + CH<sub>4</sub> reaction, we plot the cross sections as a function of total energy (sum of  $E_{coll}$  and vibra-

tional excitation energy) in Fig. 7. As seen in Fig. 7, excitation of any vibrational mode significantly enhances the reactivity relative to the  $Br + CH_4(v = 0)$  reaction. The vibrational enhancement is substantial even at low collision energies, which is different from the similar late-barrier Cl +  $CH_4/CHD_3$  reaction.<sup>15, 19, 24, 58</sup> Figure 7 nicely demonstrates that chemical reactivity depends on the distribution of the initial total energy, since at the same total energy the reactivity is quite different if the energy is deposited into translation or vibration. Furthermore, not all the vibrational modes of the polyatomic reactants are equally efficient to help the reaction to surmount the barrier. Clearly, the stretching modes of CH<sub>4</sub> have more substantial enhancement effects than the bending/umbrella modes. Overall, the late-barrier  $Br + CH_4$ reaction is a good example where the extended Polanyi rules hold.

We have investigated the effect of the SO correction on the dynamics by comparing the cross sections of the Br(<sup>2</sup>P) + CH<sub>4</sub>(v = 0) and Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>(v = 0) reactions as shown in Figure 8. Since the SO correction effectively increases the



FIG. 7. Cross sections as a function of total energy [sum of the collision energy and the vibrational energy relative to  $CH_4(v = 0)$ ] for the ground-state (v = 0), bending-excited ( $v_4$  and  $v_2$ ), and stretching-excited ( $v_1$  and  $v_3$ )  $Br(^2P_{3/2}) + CH_4(v_k = 0, 1)$  [k = 1, 2, 3, 4] reactions obtained by considering all trajectories without ZPE constraint or weighting.



FIG. 8. Cross sections as a function of collision energy for the Br(<sup>2</sup>P) + CH<sub>4</sub>(v = 0) and Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>(v = 0) reactions obtained by using the non-SO and SO PESs, respectively, considering all trajectories without ZPE constraint or weighting.



FIG. 9. Reaction probabilities as a function of impact parameter for the ground-state (v = 0), bending-excited ( $v_4$  and  $v_2$ ), and stretching-excited ( $v_1$  and  $v_3$ ) Br( $^{2}P_{3/2}$ ) + CH<sub>4</sub>( $v_k = 0, 1$ ) [k = 1, 2, 3, 4] reactions at different collision energies obtained by considering all trajectories without ZPE constraint or weighting.

barrier height by 1228 cm<sup>-1</sup>, we can expect larger cross sections on the non-SO PES. Indeed, the non-SO cross sections are 3-5 times larger than the SO ones. The SO effect on the  $Br + CH_4$  reaction is significantly larger than that on the Cl + CH<sub>4</sub> reaction.<sup>16</sup> For the latter, the SO correction decreases the cross sections by a factor of 1.5-2.5 at low collision energies and the non-SO/SO cross section ratios are only 1.0-1.2 above  $E_{\text{coll}} = 10\ 000\ \text{cm}^{-1}$ .<sup>16</sup> For Br + CH<sub>4</sub>, the rapid decay of the non-SO/SO cross section ratios with increasing  $E_{\text{coll}}$  is not seen; the ratios are 4–5 at low  $E_{\text{coll}}$  and still close to 3 at  $E_{\text{coll}} = 16\,000 \text{ cm}^{-1}$ . The fact that an energy shift of 1228 cm<sup>-1</sup> can cause large effects on the cross sections at high  $E_{\text{coll}}$  is not surprising, because the enhancement factors of the bending modes, excitation energies of  $1300-1600 \text{ cm}^{-1}$ , are similar to the non-SO/SO cross section ratios. Of course, it is interesting to find that the neglect of the SO correction behaves as an internal energy excitation. This indicates that one cannot neglect the SO effect in the title reaction, especially for thermal rate calculations.

The reaction probabilities as a function of impact parameter for the Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>( $v_k = 0, 1$ ) [k = 1, 2, 3, 4] reactions at collision energies of 8000, 12 000, and 16 000 cm<sup>-1</sup> are given in Fig. 9. The reaction probabilities are very small, especially for the ground-state reaction. The value of P(b = 0) for Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>(v = 0) is only 0.0003 at  $E_{coll}$ = 8000 cm<sup>-1</sup> and it increases to 0.0036 at  $E_{coll}$ = 16 000 cm<sup>-1</sup>. It means that only about 0.36% of the trajectories are reactive at a high  $E_{coll}$  of 16 000 cm<sup>-1</sup> without applying any ZPE constraint, which would further decrease the reactivity. For comparison, at the same  $E_{coll}$  and with the same QCT analysis, P(b = 0) is more than 10% for the Cl(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>(v = 0) reaction.<sup>16</sup> The maximum impact parameter is about 4–5 bohrs for the Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>(v = 0) reaction, and significantly higher, about 6 bohrs for the stretching-excited reactions. The enhancement of the reactivity upon vibrational excitations is seen in Fig. 9, in accord with the cross section data discussed above.

Differential cross sections for the  $Br(^{2}P_{3/2}) + CH_{4}(v_{k})$ = 0, 1 [k = 1, 2, 3, 4] reactions at different collision energies are shown in Figs. 10 and 11. For the ground-state reaction backward scattering is the dominant mechanism, especially at higher collision energies. For the bending/umbrella excited reactions the products are scattered at every direction with similar probabilities, whereas for the stretching-excited reactions a clear preference toward forward scattering is seen. These angular distributions are consistent with the impact parameter dependence of the reaction probabilities, since the maximum impact parameters significantly increase upon vibrational excitations. For the  $Cl(^{2}P_{3/2}) + CH_{4}(v = 0)$  reaction we found a dramatic shift of the angular distributions from backward to forward directions with increasing collision energy.<sup>59</sup> In the case of the  $Br(^{2}P_{3/2}) + CH_{4}(v = 0)$  reaction the collision energy dependence of the angular distributions is less significant. This finding may be explained by the fact that the threshold energy for the title reaction is significantly higher than that of  $Cl + CH_4$ ; thus, the latter could be studied at much lower collision energies than the former. Indeed, the  $Cl + CH_4(v = 0)$  reaction was clearly backward scattered at an  $E_{\text{coll}}$  of around 1300 cm<sup>-1</sup>,<sup>59</sup> whereas we consider more than 6 times larger collision energies for  $Br + CH_4(v = 0)$ .



FIG. 10. Differential cross sections for the ground-state (v = 0), bending-excited ( $v_4$  and  $v_2$ ), and stretching-excited ( $v_1$  and  $v_3$ ) Br(<sup>2</sup>P<sub>3/2</sub>) + CH<sub>4</sub>( $v_k = 0, 1$ ) [k = 1, 2, 3, 4] reactions at different collision energies obtained by considering all trajectories without ZPE constraint or weighting.



FIG. 11. Differential cross sections as in Fig. 10, but each panel corresponds to different state-specific  $Br(^{2}P_{3/2}) + CH_{4}(v_{k} = 0, 1)$  [k = 1, 2, 3, 4] reactions.

#### V. SUMMARY AND CONCLUSIONS

We have developed the first *ab initio* full-dimensional PESs for the non-SO and SO ground electronic states of the Br + CH<sub>4</sub>  $\rightarrow$  HBr + CH<sub>3</sub> reaction. Furthermore, we have computed benchmark data for the controversial thermochemistry of the title reaction employing the composite FPA approach.<sup>32,33</sup> The present FPA computations provide all-electron relativistic CCSDT(Q)/complete-basis-set qual-

ity results with realistic uncertainties. Without ZPE the new benchmark energies clearly show that the barrier is below the HBr + CH<sub>3</sub> asymptote by 625 cm<sup>-1</sup>, and vdW complexes, CH<sub>3</sub>–HBr and CH<sub>3</sub>–BrH, exist with  $D_e$  values of 799 ± 10 and 344 ± 10 cm<sup>-1</sup>, respectively. If the substantial ZPE corrections are included, the barrier of the HBr + CH<sub>3</sub> reaction is only slightly below the reactants by 108 cm<sup>-1</sup>, and the  $D_0$ values of the above complexes are only 319 and 88 cm<sup>-1</sup>, respectively. The uncertainty of these ZPE corrected results is larger than that of the classical results, because the ZPEs were obtained by using the harmonic approximation.

The analytical non-SO and SO PESs were obtained by fitting 21 574 high-quality ab initio energy points using the permutationally invariant polynomial approach.<sup>12,13</sup> We found that the correlation of all the electrons and the use of the CCSD(T) method and a triple-zeta quality basis are essential to achieve accuracy better than 0.5 kcal/mol  $(175 \text{ cm}^{-1})$ . Thus, the energy points were computed by an efficient composite method based on explicit all-electron ECP-UCCSD(T)/aug-cc-pwCVDZ-PP and ECP-UMP2/augcc-pwCV*n*Z-PP [n = D and T] computations. This composite method is shown to agree with the highly accurate AE-ECP-UCCSD(T)/aug-cc-pwCVQZ-PP energies within our target accuracy of 0.5 kcal/mol. The significant scalar relativistic effects were treated by using a relativistic effective core potential for Br. The SO effects were considered as additive corrections to the non-SO composite energies. The geometry dependent SO corrections were obtained at 3127 entrancechannel configurations (excluding 2000 fragment data) with MRCI+Q computations using the interacting states approach. The analytical PESs accurately describe the vdW complexes in the entrance and product channels as well as the first-order saddle point of the title reaction. The classical barrier height and endothermicity are 7285 and 7867  $cm^{-1}$  on the SO PES, in excellent agreement with the benchmark values of 7232  $\pm$  50 and 7857  $\pm$  50 cm<sup>-1</sup>, respectively.

The mode-selective dynamics of the  $Br + CH_4$  reaction was investigated by running more than 13 million quasiclassical trajectories on the new non-SO and SO PESs. The Polanyi rules hold for this late-barrier polyatomic reaction, since the vibrational excitations are much more efficient to activate the reaction than translation energy. We found that excitations of the bending/umbrella modes by one quantum enhance the reactivity by a factor of 3-7 in the collision energy range of  $8000-16\,000 \text{ cm}^{-1}$  and the stretching modes have an order of magnitude larger enhancement factors. If the PES does not include the SO corrections, the cross sections of the Br +  $CH_4(v = 0)$  reaction are about 3–4 times larger than those on the SO PES at collision energies about two times higher than the barrier height. This SO effect is much more significant than that in the  $Cl + CH_4$  reaction. Another notable difference between the Br and  $Cl + CH_4$  reactions is that the reactivity of the title reaction is about two orders of magnitude smaller than that of the  $Cl + CH_4$  reaction. The differential cross sections of the  $Br + CH_4$  reaction show mainly backward scattering for the ground-state reaction and a preference toward forward directions for the reactant stretching-excited reactions, in accord with the increase of the maximum impact parameter upon stretching excitations.

The present PES development opens the door for many future reactive scattering calculations and can inspire experimental investigations for the Br + methane reaction complementing the previous work on the F, Cl, and O + methane reactions. Future work may study the isotope effects in the title reaction as well as the quantum effects, e.g., tunneling and reactive resonances, by performing reduced-dimensional wave packet computations. We also plan to study the HBr + CH<sub>3</sub> reaction, since the effect of the negative barrier and the influence of the vdW complex(es) in the HBr + CH<sub>3</sub> channel on the dynamics and kinetics are still open questions. The investigation of the validity of the extended Polanyi rules for an "early-negative-barrier" polyatomic reaction would also be of great interest.

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