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PAPER

# An *ab initio* spin–orbit-corrected potential energy surface and dynamics for the F + CH<sub>4</sub> and F + CHD<sub>3</sub> reactions

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We report an analytical *ab initio* three degrees of freedom (3D) spin–orbit-correction surface for the entrance channel of the F + methane reaction obtained by fitting the differences between the spin–orbit (SO) and non-relativistic electronic ground state energies computed at the MRCI+Q/aug-cc-pVTZ level of theory. The 3D model surface is given in terms of the distance,  $R(\text{C–F})$ , and relative orientation, Euler angles  $\phi$  and  $\theta$ , of the reactants treating CH<sub>4</sub> as a rigid rotor. The full-dimensional (12D) “hybrid” SO-corrected potential energy surface (PES) is obtained from the 3D SO-correction surface and a 12D non-SO PES. The SO interaction has a significant effect in the entrance-channel van der Waals region, whereas the effect on the energy at the early saddle point is only  $\sim 5\%$  of that at the reactant asymptote; thus, the SO correction increases the barrier height by  $\sim 122\text{ cm}^{-1}$ . The 12D quasiclassical trajectory calculations for the F + CH<sub>4</sub> and F + CHD<sub>3</sub> reactions show that the SO effects decrease the cross sections by a factor of 2–4 at low collision energies and the effects are less significant as the collision energy increases. The inclusion of the SO correction in the PES does not change the product state distributions.

## I. Introduction

During the past two decades the F + H<sub>2</sub> (D<sub>2</sub>, HD) abstraction reaction became a prototype of gas-phase collision dynamics.<sup>1–10</sup> Recently, the more complex F + methane (CH<sub>4</sub>, CHD<sub>3</sub>, etc.) reaction has attracted a lot of attention and has become a benchmark system for studying polyatomic reactivity.<sup>11–20</sup> The electronic ground state of both reaction systems is an open-shell doublet. Furthermore, in both cases one should deal with the fact that within a correct relativistic description the ground state of the F atom (<sup>2</sup>P) is split by  $\varepsilon = 404\text{ cm}^{-1}$  into ground (<sup>2</sup>P<sub>3/2</sub>) and excited (<sup>2</sup>P<sub>1/2</sub>) spin–orbit (SO) states. Since <sup>2</sup>P<sub>3/2</sub> and <sup>2</sup>P<sub>1/2</sub> states are 4- and 2-fold degenerate, respectively, the SO ground state lies  $\varepsilon/3 = 135\text{ cm}^{-1}$  below the non-relativistic (spin-averaged) ground state of the F atom. Within the Born–Oppenheimer (BO) approximation,<sup>21</sup> F\*(<sup>2</sup>P<sub>1/2</sub>) does not correlate with electronically ground state products. Furthermore, when the reactants approach each other the 4-fold degenerate <sup>2</sup>P<sub>3/2</sub> state is split into 2 doubly degenerate states and only one of them correlates adiabatically with ground state products. Thus, 3 doubly degenerate SO states are involved in the dynamics and within an adiabatic approach only the SO ground state is reactive.

For the F + H<sub>2</sub> reaction high-precision potential energy surfaces (PESs) for the three SO states were developed<sup>7</sup> since

the early work of Stark and Werner (SW),<sup>1</sup> who published the first high-quality non-SO PES in 1996. The dynamics of the F + H<sub>2</sub> and its isotopologue analogue reactions have been studied by quasiclassical and quantum methods based on (a) the adiabatic approach using either a single non-relativistic or a single SO ground state PES as well as (b) the nonadiabatic technique coupling three PESs (see, e.g., ref. 3–6). Aoiz *et al.*<sup>8</sup> found that the SW PES gave rate constants in very good agreement with experiment. The computations on the Hartke–Stark–Werner (HSW) PES (ref. 1 and 9), which includes SO correction in the entrance channel, underestimated the rate constants indicating that the barrier height is too high on the HSW PES. Earlier studies showed that the dynamics could be well described adiabatically on a single ground state PES and F(<sup>2</sup>P<sub>3/2</sub>) is at least 10 times more reactive than F\*(<sup>2</sup>P<sub>1/2</sub>).<sup>10</sup> However, recently evidence was found for significant excited SO state reactivity at very low collision energies ( $< 0.5\text{ kcal mol}^{-1}$ ), e.g., at  $0.25\text{ kcal mol}^{-1}$  F\*(<sup>2</sup>P<sub>1/2</sub>) is  $\sim 1.6$  times more reactive than F(<sup>2</sup>P<sub>3/2</sub>).<sup>5,6</sup> In this special low collision energy case the multiple-surface computations give significantly larger cross sections than the single PES simulations, but as the collision energy increases, the BO-allowed reaction rapidly dominates.<sup>5,6</sup>

In the case of the F + methane reaction a full-dimensional ground state PES without SO correction has been developed;<sup>17</sup> however, relativistic *ab initio* studies have not been performed apart from our<sup>17</sup> recent computations at the stationary points. In 2005 Espinosa-García and co-workers<sup>15</sup> constructed a semi-empirical SO PES, where the experimentally known SO

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splitting of the F atom was taken into account during the optimization of the PES parameters to experimental thermal rate constants. Since their semi-empirical non-SO surface (taking the spin-averaged energy as the reference level of the reactants during the calibration) gave slightly better rate constants, they continued to use and further improve<sup>16</sup> the non-SO PES.

In this paper we report the first *ab initio* study of the SO ground state PES for the F + methane reaction utilizing a physically motivated 3 degrees of freedom (3D) model as described in Section II. We perform full-dimensional quasiclassical trajectory (QCT) calculations for the F + CH<sub>4</sub> and F + CHD<sub>3</sub> reactions using (a) our recent high-quality full-dimensional (12D) *ab initio* non-SO PES (ref. 17) as well as (b) a “hybrid” SO PES in full dimensions using the 12D non-SO PES and estimating the SO effects employing the newly developed 3D SO-correction surface. The effects of the SO corrections are discussed in Section III. Finally, we note that we are aware of the fact that adiabatic QCT calculations on the SO ground state PES may not be sufficient to correctly describe the dynamics (especially at low collision energies); however, multiple-surface dynamics is out of the scope of the present study.

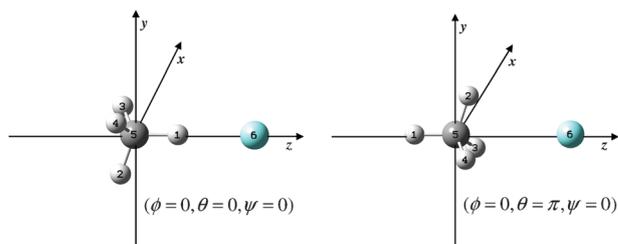
## II. Spin-orbit-corrected potential energy surface

### A The 3 degrees of freedom model

Let us define the SO correction as the difference between electronic energies of the lowest SO state and the non-relativistic electronic ground state. As already noted, this correction at the reactant asymptote is  $-135\text{ cm}^{-1}$ , whereas, as our previous computation shows,<sup>17</sup> the SO correction is only  $-8.1\text{ cm}^{-1}$  at the early saddle point, which has a reactant like structure. These values show that the SO effect tends to vanish as the F atom approaches CH<sub>4</sub>, similar to the F + H<sub>2</sub> system. Also SO coupling is minor in the product channels; thus, the SO interaction plays a significant role only in the entrance channel of the F + CH<sub>4</sub> reaction. Therefore, a 3D model considering the intermolecular coordinates of the reactants seems to be reasonable for describing the SO surface of the F + CH<sub>4</sub> reaction (see Fig. 1). We keep the 9 internal coordinates of CH<sub>4</sub> fixed at their equilibrium values and we use the C–F distance ( $R$ ) and two Euler angles ( $\phi, \theta$ ) as variables of the SO-correction surface. In this study we use the so-called convention  $z$ - $x$ - $z$  to define the Euler angles. In this convention, the orientation of CH<sub>4</sub> is described by three rotations about the reference space-fixed frame ( $xyz$ ). The first rotation is about the  $z$ -axis by  $\phi \in [0, 2\pi]$ , the second is about the  $x$ -axis by  $\theta \in [0, \pi]$ , and the third is about the  $z$ -axis (again) by  $\psi \in [0, 2\pi]$ . Since the F atom is fixed at Cartesian coordinates  $(0, 0, R)$ , *i.e.*, F is on the  $z$ -axis, the final rotation about the  $z$ -axis does not change any internuclear distances; therefore, the SO interaction does not depend on  $\psi$ . The orientation of CH<sub>4</sub> in the reference frame at zero Euler angles is shown in Fig. 1.

### B Computational details

We set up a direct-product grid of  $R$  ( $\text{\AA}$ ) = {2.0, 2.4, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.4, 3.6, 4.0, 6.0, 10.0},  $\phi$  ( $^\circ$ ) = {0, 30, 60, ..., 360}, and  $\theta$  ( $^\circ$ ) = {0, 20, 40, ..., 180}. At each



**Fig. 1** The 3 degrees of freedom ( $R, \phi, \theta$ ) model of CH<sub>4</sub>...F, where the orientation of the rigid CH<sub>4</sub>(eq) is given by two Euler angles ( $\phi, \theta$ ) and the F atom is fixed at Cartesian coordinates  $(0, 0, R)$  in the space-fixed frame ( $xyz$ ). The Euler angles describe rotations about the axes  $z, x$ , and  $z$  by  $\phi, \theta$ , and  $\psi$ , in order. The final rotation about the  $z$ -axis (the C...F axis) does not change any interatomic distances; thus, the spin-orbit correction does not depend on  $\psi$ .

3D grid point we performed multi-reference configuration interaction (MRCI+Q)<sup>22</sup> computations with the aug-cc-pVTZ basis set<sup>23</sup> using a minimal active space of 5 electrons in the 3 spatial 2p-like orbitals corresponding to the F atom. The Davidson correction<sup>24</sup> (+Q) was utilized to estimate the effect of the higher-order excitations. We employed the usual frozen-core approach for the electron correlation computations; *i.e.*, the 1s-like core orbitals corresponding to the C and F atoms were kept frozen. The SO eigenstate calculations employed the Breit–Pauli operator in the interacting-states approach<sup>25</sup> using the Davidson-corrected MRCI energies as the diagonal elements of the  $6 \times 6$  SO matrix. All the electronic structure computations were performed by the *ab initio* program package MOLPRO.<sup>26</sup>

### C Fitting the spin-orbit-correction energies

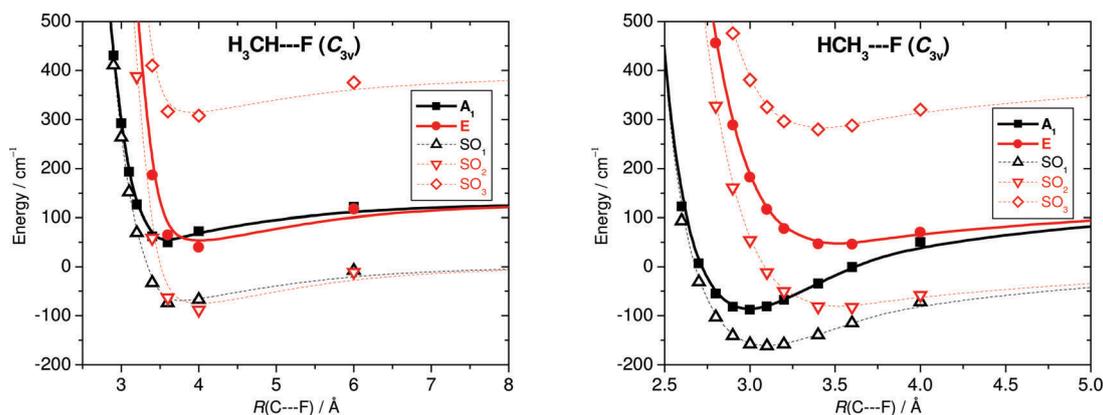
The analytical representation of the SO-correction surface has the functional form

$$V^{\text{SO}}(R, \phi, \theta) = \sum_{n=0}^N \sum_{k=0}^K \chi_n(R) \cos(3k\phi) \left( \sum_{l=0}^L a_{nkl} \cos(l\theta) + \sum_{m=1}^M b_{nkm} \sin(m\theta) \right), \quad (1)$$

where

$$\chi_0(R) = 1 \text{ and } \chi_n(R) = \tanh[n \times c(R - R_0)] \text{ if } n = 1, 2, 3, \dots \quad (2)$$

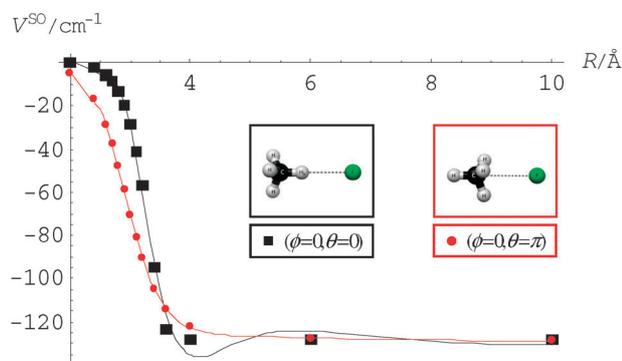
The coefficients  $a_{nkl}$  and  $b_{nkm}$  have been determined by a linear least-squares fit to the *ab initio* data. We set  $N = 6$ ,  $K = 2$ , and  $L = M = 3$ ; thus, the total number of coefficients is  $(N + 1) \times (K + 1) \times (L + M + 1) = 147$ . After several test fits, the nonlinear parameters were fixed at  $c = 0.42\text{ \AA}^{-1}$  and  $R_0 = 2.3\text{ \AA}$ . Using the above parameters the root-mean-square fitting error is  $1.7\text{ cm}^{-1}$ . It is important to note that due to the  $C_{3v}$  symmetry of CH<sub>4</sub>...F at  $\theta = 0$  (see Fig. 1)  $V^{\text{SO}}$  has to be a periodic function along  $\phi$  with period  $120^\circ$ , *i.e.*,  $V^{\text{SO}}(R, \phi + 120^\circ, \theta) = V^{\text{SO}}(R, \phi, \theta)$ . As seen in eqn (1), this periodicity is explicitly built in the functional form of the fitting basis.



**Fig. 2** Potential energy curves of  $\text{CH}_4 \cdots \text{F}$  as a function of the  $\text{C} \cdots \text{F}$  distance along the  $C_{3v}$  axis with fixed equilibrium  $\text{CH}_4$  geometry and  $\text{C}-\text{H} \cdots \text{F}$  (left panel) and  $\text{H}-\text{C} \cdots \text{F}$  (right panel) linear bond arrangements computed at the frozen-core MRCI+Q/aug-cc-pVTZ level using a minimal active space.  $A_1$  and  $E$  denote the ground and excited non-relativistic electronic states, respectively.  $SO_1$ ,  $SO_2$ , and  $SO_3$  are the three spin-orbit states. The energies are relative to  $\text{F}(^2P_{3/2}) + \text{CH}_4(\text{eq})$ .

### D Properties of the spin-orbit-correction energy surface

Potential energy curves of  $\text{CH}_4 \cdots \text{F}$  along the  $C_{3v}$  axis are shown in Fig. 2. In the case of  $C_{3v}$  point-group symmetry there are two non-relativistic electronic states,  $^2A_1$  and  $^2E$ . Only  $^2A_1$  state correlates adiabatically with products in their electronic ground states. When the SO coupling is considered, the  $^2E$  state splits into two SO states and neither of these two SO states give ground state products. In the case of  $\text{C}-\text{H} \cdots \text{F}$  configurations there is a shallow van der Waals (vdW) well around  $R(\text{CF}) = 3.5\text{--}3.8 \text{ \AA}$  below the reactant asymptote by about  $40\text{--}90 \text{ cm}^{-1}$  (high sensitivity to the level of theory). The SO coupling has negligible effect on this relative energy. Note that the energies of the  $^2A_1$  and  $^2E$  states as well as the two lowest energy SO states are very close to each other at this region and the  $^2E$  potential crosses the  $^2A_1$  (see the left panel of Fig. 2). On the other hand, in the case of the  $\text{H}-\text{C} \cdots \text{F}$  bond arrangements the separation between the  $^2A_1$  and  $^2E$  states is larger and there is no crossing (see the right panel of Fig. 2). The  $^2E$  state has only a shallow vdW well around  $R(\text{CF}) = 3.5 \text{ \AA}$ , whereas the  $^2A_1$  potential has a significantly deeper minimum at about  $R(\text{CF}) = 3.0 \text{ \AA}$  with  $D_e = 200\text{--}250 \text{ cm}^{-1}$ . The SO effect is important in this well, since it decreases the depth of the vdW well by about  $50 \text{ cm}^{-1}$ .



**Fig. 3** One-dimensional cuts of the spin-orbit-correction surface of  $\text{CH}_4 \cdots \text{F}$  as a function of the  $\text{C} \cdots \text{F}$  distance ( $R$ ) along the  $C_{3v}$  axis at  $\theta = 0$  and  $180^\circ$ . The curves are the fitted functions [eqn (1)], whereas the points represent the *ab initio* data.

One-dimensional cuts of the SO-correction surface along the  $C_{3v}$  axis are shown in Fig. 3. At  $10 \text{ \AA}$   $\text{C}-\text{F}$  separation the SO correction tends to its asymptotic value of  $-129 \text{ cm}^{-1}$  at the MRCI+Q/aug-cc-pVTZ (minimal active space) level of theory. This result is in good agreement with the accurate value of  $-135 \text{ cm}^{-1}$  obtained from the experimental SO splitting. (Note that the MRCI+Q/aug-cc-pVDZ (minimal active space) level gives  $-120 \text{ cm}^{-1}$ .) The SO effect starts to decrease around  $R(\text{CF}) = 4 \text{ \AA}$  and tends to vanish at about  $R(\text{CF}) = 2 \text{ \AA}$ . The SO corrections are larger (in absolute value) at  $\text{H}-\text{C} \cdots \text{F}$  bond arrangement than at  $\text{C}-\text{H} \cdots \text{F}$ . The largest difference is  $41 \text{ cm}^{-1}$  at  $R(\text{CF}) = 3 \text{ \AA}$ , *i.e.*,  $-70$  and  $-29 \text{ cm}^{-1}$ , respectively. Thus, it is clear that the SO effect depends sensitively on the orientation of  $\text{CH}_4$  especially in the vdW region.

Fig. 4 shows two-dimensional cuts of the SO-correction surface as a function of  $\phi$  and  $\theta$  at fixed  $\text{C} \cdots \text{F}$  distances of  $2.63$  and  $3.00 \text{ \AA}$ . The former distance corresponds to the saddle-point region and the latter represents the above-mentioned vdW well of the PES. The shapes of the two surfaces are similar; however, the SO corrections are in the ranges  $[-6, -31]$  and  $[-29, -70] \text{ cm}^{-1}$  in the saddle-point and vdW regions, respectively. The SO effects are the largest at  $\theta = 180^\circ$  ( $\text{H}-\text{C} \cdots \text{F}$ ) and the smallest at  $\theta = 0$  ( $\text{C}-\text{H} \cdots \text{F}$ ). The  $\text{H}-\text{C} \cdots \text{F}$  vdW minimum ( $C_{3v}$ ) corresponds to  $\theta = 180^\circ$  ( $R \approx 3.00 \text{ \AA}$ ), *i.e.*,  $V^{\text{SO}} \approx -70 \text{ cm}^{-1}$ , whereas the bent saddle point ( $C_s$ ) is at  $\phi = 60^\circ$  and  $\theta \approx 20^\circ$  ( $R \approx 2.63 \text{ \AA}$ ), *i.e.*,  $V^{\text{SO}} \approx -7 \text{ cm}^{-1}$ . One can observe several relations, which come from the symmetry of the model system:

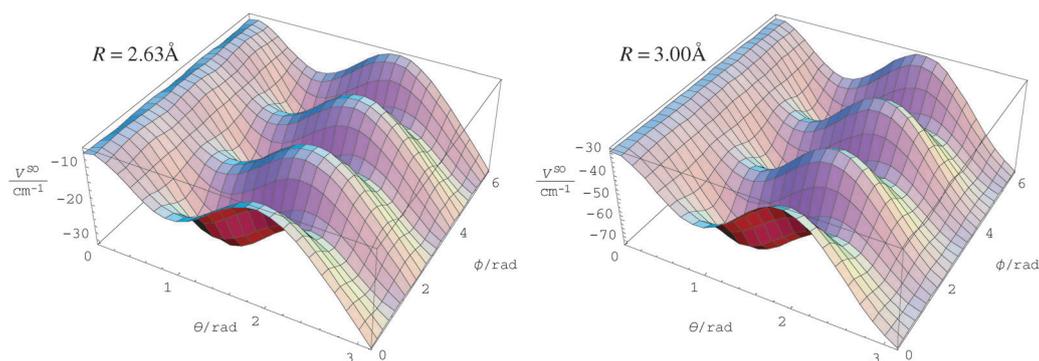
(a) at  $\theta = 0$  and  $180^\circ$  the SO correction does not depend on  $\phi$ ;

$$(b) V^{\text{SO}}(R, \phi + 120^\circ, \theta) = V^{\text{SO}}(R, \phi, \theta);$$

$$(c) V^{\text{SO}}(R, \phi = 0, \theta = 109.5^\circ) = V^{\text{SO}}(R, \phi = 0, \theta = 0); \text{ and}$$

$$(d) V^{\text{SO}}(R, \phi = 60^\circ, \theta = 70.5^\circ) = V^{\text{SO}}(R, \phi, \theta = 180^\circ).$$

[Note that  $70.5^\circ = 180^\circ - 109.5^\circ$  (tetrahedral symmetry of the  $\text{CH}_4$  unit).] Of course, (b) can be combined with (c) and (d). As already noted, (b) is explicitly considered in the functional form of the surface [see eqn (1)]. Furthermore, as Fig. 4 shows, (a), (c), and (d) are numerically well satisfied.



**Fig. 4** Two-dimensional cuts of the spin-orbit-correction surface of  $\text{CH}_4 \cdots \text{F}$  as a function of  $\phi$  and  $\theta$  at fixed  $\text{C} \cdots \text{F}$  distances of 2.63 Å (saddle-point region) and 3.00 Å (van der Waals region). See Fig. 1 for the definition of the Euler angles.

### E The full-dimensional spin-orbit-corrected potential energy surface

The full-dimensional SO ground state surface in terms of Cartesian coordinates of  $\text{F} + \text{CH}_4$  is obtained as a “hybrid” of the 12D non-SO PES ( $V^{12\text{D}}$ ) and the 3D SO-correction surface [eqn (1)] as follows:

(1) Let us translate and rotate the Cartesian coordinates to the frame where the C atom is in the origin and the coordinates of the F atom are  $(0, 0, R)$ , where  $R$  is the C–F distance. The Cartesian coordinates in this frame are denoted as  $\mathbf{r}_i$  where  $\mathbf{r}_i = (x_i, y_i, z_i)$  and  $i = 1\text{--}4(\text{H}), 5(\text{C}),$  and  $6(\text{F})$  [see the atom numbering in Fig. 1].

(2) The Euler angles  $\theta$  and  $\phi$  are obtained as

$$\theta = \arccos\left(\frac{z_1}{\sqrt{x_1^2 + y_1^2 + z_1^2}}\right) \quad (3)$$

and

$$\phi = \arccos\left(\frac{z_2 - R_{\text{CH}_2} \cos \theta \cos \alpha}{R_{\text{CH}_2} \sin \theta \sin \alpha}\right), \quad (4)$$

where  $R_{\text{CH}_2} = \sqrt{x_2^2 + y_2^2 + z_2^2}$  and  $\alpha$  is the  $\text{H}_1\text{--C--H}_2$  bond angle of the 12D  $\text{FCH}_4$ .

(3) Finally, the SO-corrected potential energy is obtained as  $V^{12\text{D}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_6) + V^{\text{SO}}(R, \phi, \theta)$  if  $\min(R_{\text{FH}_i}) > 1.4$  Å (entrance channel). If the above condition is not true (product channel), then  $V^{\text{SO}}(R, \phi, \theta) = 0$  and only the non-SO PES is used. (Note that 1.4 Å is less than the  $\text{H} \cdots \text{F}$  distance at the saddle point and larger than the maximum classical vibrational amplitude of the  $\text{HF}$  ( $v \leq 4$ ) molecule.)

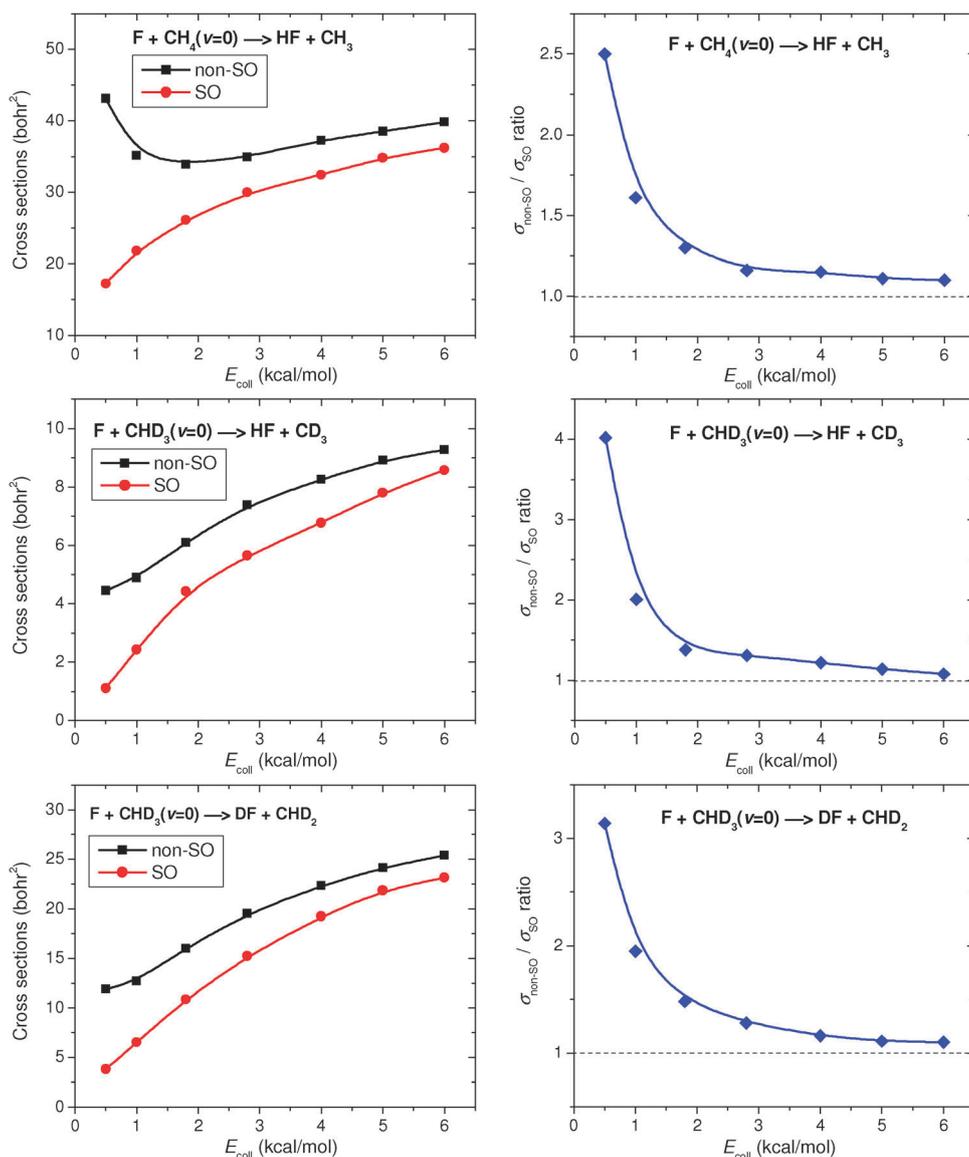
It is important to note that the above expressions are only exact if the  $\text{CH}_4$  unit is in equilibrium. Since  $\text{CH}_4$  is just slightly distorted in the entrance channel of the reaction, the above equations remain a good approximation. As described above, the new 3D SO-correction surface can be interfaced to any full-dimensional non-SO  $\text{F} + \text{CH}_4$  PES and can also be employed in direct dynamics, where the non-SO PES is computed “on-the-fly”.

### III. Quasiclassical trajectory calculations on the spin-orbit-corrected potential energy surface

We have performed QCT calculations for the  $\text{F} + \text{CH}_4(v=0)$  and  $\text{F} + \text{CHD}_3(v=0)$  reactions using (a) a non-SO full-dimensional *ab initio* PES from ref. 17 and (b) a SO ground state surface as a “hybrid” of (a) and the newly developed SO-correction surface as described in Section II. E. The SO correction has no effect on the product channel of the reaction, but it modifies the entrance channel of the PES. The saddle-point barrier height is  $167 \text{ cm}^{-1}$  on the non-SO PES,<sup>17</sup> whereas on the SO surface the barrier is at  $289 \text{ cm}^{-1}$  relative to  $\text{F}^2(\text{P}) + \text{CH}_4(\text{eq})$  and  $\text{F}^2(\text{P}_{3/2}) + \text{CH}_4(\text{eq})$ , respectively. The saddle-point structure is virtually not affected by the SO correction. Since the SO effect shifts the reactant asymptote of the PES by  $-129 \text{ cm}^{-1}$ , the reaction is less exothermic on the SO-corrected surface, *i.e.*, the equilibrium reaction enthalpies on the non-SO and SO PESs are  $-9784$  and  $-9655 \text{ cm}^{-1}$ , respectively.

The QCT calculations employed standard normal mode sampling<sup>27</sup> and usual velocity adjustment to set the angular momentum of methane to zero. The initial separation between the reactants was  $\sqrt{x^2 + b^2}$ , where  $b$  is the impact parameter and  $x$  was set to 10 bohr. Trajectories were run at seven different collision energies ( $E_{\text{coll}}$ ), *i.e.*, 0.5, 1.0, 1.8, 2.8, 4.0, 5.0, and 6.0  $\text{kcal mol}^{-1}$ . The impact parameter was varied by 1 bohr steps from 0 to  $b_{\text{max}}$ , where  $b_{\text{max}}$  was 9 bohr at 0.5 and 1.0  $\text{kcal mol}^{-1}$  and 7 bohr at the larger  $E_{\text{coll}}$ . 5000 trajectories were computed at each  $b$ , *i.e.*, 50 000 or 40 000 trajectories at each  $E_{\text{coll}}$ . The integration step was 0.0726 fs and the trajectories were propagated for a maximum of 20 000 steps (30 000 at the lowest two  $E_{\text{coll}}$ ).

Total cross sections of the  $\text{F} + \text{CH}_4(v=0)$  and  $\text{F} + \text{CHD}_3(v=0)$  reactions as a function of collision energy are shown in Fig. 5. The SO correction has a significant effect on the cross sections at low  $E_{\text{coll}}$ . At  $E_{\text{coll}} = 0.5 \text{ kcal mol}^{-1}$  the  $\sigma_{\text{non-SO}}/\sigma_{\text{SO}}$  cross-section ratio is about 2.5 for the  $\text{F} + \text{CH}_4(v=0)$  reaction and even larger, 4.0 (HF channel) and 3.1 (DF channel), in the case of the  $\text{F} + \text{CHD}_3(v=0)$  reaction. As the collision energy increases the  $\sigma_{\text{non-SO}}/\sigma_{\text{SO}}$  ratio tends to 1, *e.g.*,  $\sigma_{\text{non-SO}}/\sigma_{\text{SO}}$  is about 1.1 at  $E_{\text{coll}} = 6.0 \text{ kcal mol}^{-1}$ . The larger SO effects on the low- $E_{\text{coll}}$  cross sections of the  $\text{F} + \text{CHD}_3(v=0)$  reaction may be explained by the smaller vibrational zero-point energy (ZPE) of  $\text{CHD}_3$  than



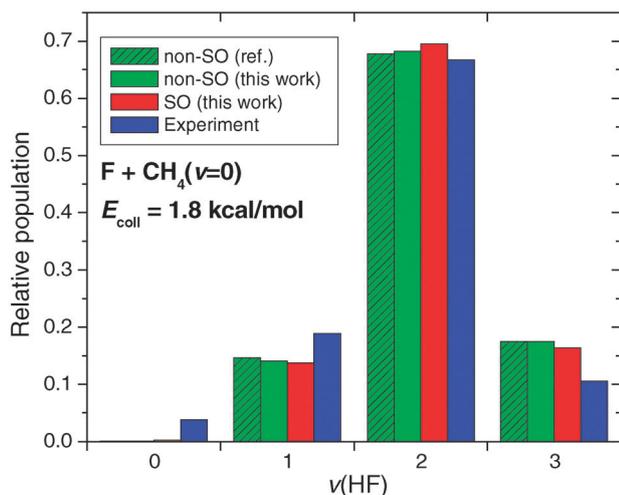
**Fig. 5** Total cross sections without ZPE constraint (left panels) of the  $F + \text{CH}_4(v=0)$  and  $F + \text{CHD}_3(v=0)$  reactions obtained from QCT calculations on (a) a non-SO PES [ref. 17] and (b) a single ground state SO surface [described in Section II. E] as well as the ratios of the non-SO and SO cross sections (right panels).

the ZPE of  $\text{CH}_4$ . Furthermore, the ZPE issue of the QCT calculations (unphysical redistribution of ZPE in the entrance channel of the reaction) can be the reason why the non-SO cross sections of the  $F + \text{CH}_4(v=0)$  reaction do not have a threshold, but  $\sigma_{\text{non-SO}}$  rather increases at lower  $E_{\text{coll}}$ . When the SO corrections are applied, *i.e.*, the barrier height is increased by  $122 \text{ cm}^{-1}$ , the excitation function has a more realistic behavior and it decreases with decreasing  $E_{\text{coll}}$ .

We have also investigated whether the SO correction has any effect on the product-state distributions of the  $F + \text{CH}_4$  reaction. Fig. 6 shows the HF vibrational populations at  $E_{\text{coll}} = 1.8 \text{ kcal mol}^{-1}$  obtained from (a) QCT calculations (ref. 17) on the non-SO PES; (b) QCT calculations (this work) on the same non-SO PES; (c) QCT calculations (this work) on the SO PES; and (d) experiment (ref. 11). All the theoretical distributions were computed with the same ZPE-constrained

binning as described in ref. 17. (a) and (b) show results from independent trajectories on the same PES indicating the statistical uncertainty of the QCT analysis. As Fig. 6 shows, the statistical error is negligible, and the HF( $v$ ) relative populations are almost the same on the non-SO and SO surfaces. As expected, the  $\sim 1\%$  SO effect on the enthalpy of the reaction does not have significant effects on the product distributions. Both the non-SO and SO HF( $v$ ) distributions are in good agreement with experiment.

Following a recent crossed molecular beam experiment,<sup>12</sup> we reported that the CH stretching excitation steers the F atom to the CD bond in the  $F + \text{CHD}_3$  reaction,<sup>18</sup> which confirmed the surprising experimental finding. This long-range stereodynamical effect is seen on the SO-corrected PES as well, and the SO correction has no significant effect on the stereodynamics. However, the SO correction has less effect on



**Fig. 6** Normalized HF( $v$ ) vibrational populations for the F + CH<sub>4</sub>( $v=0$ ) reaction at  $E_{\text{coll}} = 1.8$  kcal mol<sup>-1</sup>. The computed QCT results only consider trajectories in which the CH<sub>3</sub> product has internal energy at least ZPE. (HF never violates ZPE.) The “ref.” and experimental results are taken from ref. 17 and 11, respectively.

the cross sections of the HF channel, because the CH-stretch excitation helps to go over the increased barrier. Therefore, even if the F atom goes to one of the D atoms with very high probability (>90% at  $E_{\text{coll}} = 1$  kcal mol<sup>-1</sup>), the DF/HF product ratio is less than 3 when the SO surface is employed. Nevertheless, at  $E_{\text{coll}} = 1$  kcal mol<sup>-1</sup>, where the steering effect is the largest, the DF/HF ratio is still slightly larger in the CH stretching excited reaction than that in the F + CHD<sub>3</sub>( $v=0$ ) reaction.

#### IV. Summary and conclusions

We have developed an *ab initio* spin-orbit-correction surface for the F(<sup>2</sup>P<sub>3/2</sub>) + methane reaction. Since the spin-orbit coupling is only important in the entrance channel of the title reaction, we employed a three-dimensional model considering the three intermolecular degrees of freedom of the reactants, *i.e.*, the C–F distance and two Euler angles describing the orientation of CH<sub>4</sub>(eq). The SO correction, difference between the non-relativistic and SO ground state energies, lowers the reactant asymptote by 129 cm<sup>-1</sup> (MRCI+Q/aug-cc-pVTZ, minimal active space) and this effect begins to decrease around  $R(\text{CF}) = 4$  Å and tends to vanish at 2 Å. (The saddle-point structure corresponds to  $R(\text{CF}) \approx 2.6$  Å, where the SO correction is only about 7 cm<sup>-1</sup>.) Furthermore, the SO effect was found to be sensitive to the orientation of CH<sub>4</sub>, especially around the van der Waals region,  $R(\text{CF}) \approx 3.0$  Å, where the absolute SO correction is larger by 41 cm<sup>-1</sup> at the collinear H–C···F arrangement than at C–H···F. We have also described an implementation of the 3D SO-correction surface for full(12)-dimensional computations.

Quasiclassical trajectory calculations were performed for the F + CH<sub>4</sub> and F + CHD<sub>3</sub> reactions at seven different collision energies in order to investigate the dynamical effects of the SO correction. The SO interaction increases the barrier height by 122 cm<sup>-1</sup>, which results in a significant drop, by a

factor of 2–4, in the cross sections at low collision energies. The SO effect on the cross sections tends to vanish at higher collision energies, *e.g.*, only ~10% effect at  $E_{\text{coll}} = 6$  kcal mol<sup>-1</sup>. These results show that the low- $E_{\text{coll}}$  cross sections are highly sensitive to the barrier height and to the entrance channel of the potential energy surface indicating that the first-principles computation of the thermal rate constant of the F + methane reaction is extremely challenging. On the other hand, the SO correction has virtually no effect on the product state distributions, unless specific product states near their energetic thresholds are considered.

Finally, we note that the present study, which involves several approximations, is just a first step toward considering the SO effects in the title reaction. In the future one may develop surfaces for all the three SO states; thus, the coupling between these states could be considered during the dynamics simulations. Within the Born–Oppenheimer approximation the reaction of the SO excited F\*(<sup>2</sup>P<sub>1/2</sub>) atom is forbidden; however, in the case of the F + H<sub>2</sub> (D<sub>2</sub>) reaction there is evidence for non-adiabatic dynamics, where F\*(<sup>2</sup>P<sub>1/2</sub>) plays an important role.<sup>5,6</sup> Therefore, multiple-surface dynamics could give different results from the present ones, especially at low  $E_{\text{coll}}$ , for the F + methane reaction as well. Furthermore, experiments highlight reactive resonances (quantum effects) at low collision energies in the title reactions;<sup>13</sup> therefore, quantum dynamics may also be required to get more realistic theoretical descriptions of the reactions. The SO effects may also play an important role if one is to compute resonance states, since such a computation requires highly precise potential energy surface(s) in the entrance channel.

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