

Electronic Supplementary Information (ESI)

for

Full-dimensional potential energy surface for the H + CH₃OH reaction.

Theoretical kinetics and dynamics study.

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Potential energy surface

The new PES for the reaction of the hydrogen atom with methanol was developed in a two-step process: first, the analytical functional form was proposed, which depends on adjustable parameters, and then they were fitted to *ab initio* calculations. These steps will now be explained in detail.

a) Analytical functional form

On the basis of our previous experience with symmetrically substituted polyatomic reactions of type $A + CX_4 \rightarrow AX + CX_3$ (Ref. 1-16) or $A + C_2X_6 \rightarrow AX + C_2X_5$ (Ref. 17-20), in which the central atom, carbon, is bonded to four or six equivalent substituents, X, and A represents the attacking atom; or with asymmetrically substituted polyatomic reactions of type $A + CX_3Y \rightarrow AX/AY + CX_2Y/CX_3$ and $A + CXYZW \rightarrow \text{Products}$ (Ref. 21, 22) where the central atom, carbon, is bonded to different substituents; the new surface for reactions of type $A + CX_3OY \rightarrow AX + CX_2OY // AY + CX_3O$ is formulated in similar physically intuitive terms: stretching, valence bending, and out-of-plane bending. The main novelties of the new potential energy surface developed in the present work are: a) it has the possibility of two different central atoms; b) these two atoms can be bonded to the same or to different substituents, and c) two reactive channels can be described with only one potential energy surface, i.e., in this case we can describe the hydrogen abstraction reaction of the two different types of hydrogen presents in the methanol, methyl and hydroxyl hydrogen. Therefore, the surface is a valence-bond (VB) potential augmented with molecular mechanics (MM) terms, in brief, a VB-MM surface.

For the title reaction the potential energy for a given geometry, V , has the following general form,

$$V = V_{str} + V_{CO} + V_{bending} + V_{op} + V_{tor} \quad (S1)$$

V_{str} is the stretching term describing all C-H and O-H bonds and is given by,

$$V_{str} = \sum_{i=1}^3 V_3(R_{CX_i}, R_{CA}, R_{AX_i}) + V_3(R_{OY}, R_{OA}, R_{AY}) \quad (S2)$$

X_i stands for one of the three hydrogens bonded to the carbon atom, while Y is the hydrogen atom bonded to the oxygen. Note that although in this work, X, Y= H, in general the atoms bonded to the carbon and the oxygen atoms can be the same or different types

of atom. In addition, note that the three hydrogen atoms in C are equivalent, although we differentiate between them as i, j, k for the sake of clarity in the discussion. The V_3 terms represent the London-Eyring-Polanyi (LEP) functional form, given by,

$$\begin{aligned}
 V_3(R_{CX_i}, R_{CA}, R_{AX_i}) &= (V_{Q,CX_i} + V_{Q,CA} + V_{Q,AX_i}) \\
 &+ \left[-\frac{(V_{J,CX_i} - V_{J,CA})^2 + (V_{J,CA} - V_{J,AX_i})^2 + (V_{J,AC} - V_{J,CX_i})^2}{2} \right]^{1/2}
 \end{aligned} \tag{S3}$$

for the C atom, and

$$\begin{aligned}
 V_3(R_{OY}, R_{OA}, R_{AY}) &= (V_{Q,OY} + V_{Q,OA} + V_{Q,YA}) \\
 &+ \left[-\frac{(V_{J,OY} - V_{J,OA})^2 + (V_{J,OA} - V_{J,AY})^2 + (V_{J,AO} - V_{J,OY})^2}{2} \right]^{1/2}
 \end{aligned} \tag{S4}$$

for the O atom; where V_Q and V_J are the Coulomb and exchange integrals, respectively, given by,

$$V_{Q,CX_i} = \frac{E_{CX_i}^1 + E_{CX_i}^3}{2} \tag{S5}$$

$$V_{J,CX_i} = \frac{E_{CX_i}^1 - E_{CX_i}^3}{2} \tag{S6}$$

$$V_{Q,AX_i} = \frac{E_{AX_i}^1 + E_{AX_i}^3}{2} \tag{S7}$$

$$V_{J,AX_i} = \frac{E_{AX_i}^1 - E_{AX_i}^3}{2} \tag{S8}$$

$$V_{Q,CA} = \frac{E_{CA}^1 + E_{CA}^3}{2} \tag{S9}$$

$$V_{J,CA} = \frac{E_{CA}^1 - E_{CA}^3}{2} \tag{S10}$$

$$V_{Q,OY} = \frac{E_{OY}^1 + E_{OY}^3}{2} \tag{S11}$$

$$V_{J,OY} = \frac{E_{OY}^1 - E_{OY}^3}{2} \quad (S12)$$

$$V_{Q,AY} = \frac{E_{AY}^1 + E_{AY}^3}{2} \quad (S13)$$

$$V_{J,AY} = \frac{E_{AY}^1 - E_{AY}^3}{2} \quad (S14)$$

$$V_{Q,OA} = \frac{E_{OA}^1 + E_{OA}^3}{2} \quad (S15)$$

$$V_{J,OA} = \frac{E_{OA}^1 - E_{OA}^3}{2} \quad (S16)$$

Each V_3 term involves a singlet curve ($E_{CX_i}^1$, E_{OY}^1 , E_{CA}^1 , E_{OA}^1 , E_{AY}^1 and $E_{AX_i}^1$) and a triplet curve ($E_{CX_i}^3$, E_{OY}^3 , E_{CA}^3 , E_{OA}^3 , E_{AY}^3 and $E_{AX_i}^3$) for each bond. This singlet and triplet curves are given by

$$E_{CX_i}^1 = D_{CX_i}^1 * e^{-2\alpha_{CX_i} * (R_{CX_i} - R_{CX_i}^0)} - 2 * e^{-\alpha_{CX_i} * (R_{CX_i} - R_{CX_i}^0)} \quad (S17)$$

$$E_{CX_i}^3 = D_{CX_i}^3 * e^{-2\alpha_{CX_i} * (R_{CX_i} - R_{CX_i}^0)} + 2 * e^{-\alpha_{CX_i} * (R_{CX_i} - R_{CX_i}^0)} \quad (S18)$$

$$E_{OY}^1 = D_{OY}^1 * e^{-2\alpha_{OY} * (R_{OY} - R_{OY}^0)} - 2 * e^{-\alpha_{OY} * (R_{OY} - R_{OY}^0)} \quad (S19)$$

$$E_{OY}^3 = D_{OY}^3 * e^{-2\alpha_{OY} * (R_{OY} - R_{OY}^0)} + 2 * e^{-\alpha_{OY} * (R_{OY} - R_{OY}^0)} \quad (S20)$$

$$E_{CA}^1 = D_{CA}^1 * e^{-2\alpha_{CA} * (R_{CA} - R_{CA}^0)} - 2 * e^{-\alpha_{CA} * (R_{CA} - R_{CA}^0)} \quad (S21)$$

$$E_{CA}^3 = D_{CA}^3 * e^{-2\alpha_{CA} * (R_{CA} - R_{CA}^0)} + 2 * e^{-\alpha_{CA} * (R_{CA} - R_{CA}^0)} \quad (S22)$$

$$E_{OA}^1 = D_{OA}^1 * e^{-2\alpha_{OA} * (R_{OA} - R_{OA}^0)} - 2 * e^{-\alpha_{OA} * (R_{OA} - R_{OA}^0)} \quad (S23)$$

$$E_{OA}^3 = D_{OA}^3 * e^{-2\alpha_{OA} * (R_{OA} - R_{OA}^0)} + 2 * e^{-\alpha_{OA} * (R_{OA} - R_{OA}^0)} \quad (S24)$$

$$E_{AY}^1 = D_{AY}^1 * e^{-2\alpha_{AY} * (R_{AY} - R_{AY}^0)} - 2 * e^{-\alpha_{AY} * (R_{AY} - R_{AY}^0)} \quad (S25)$$

$$E_{AY}^3 = D_{AY}^3 * e^{-2\alpha_{AY} * (R_{AY} - R_{AY}^0)} + 2 * e^{-\alpha_{AY} * (R_{AY} - R_{AY}^0)} \quad (S26)$$

$$E_{AX_i}^1 = D_{AX_i}^1 * e^{-2\alpha_{AX_i} * (R_{AX_i} - R_{AX_i}^0)} - 2 * e^{-\alpha_{AX_i} * (R_{AX_i} - R_{AX_i}^0)} \quad (S27)$$

$$E_{AX_i}^3 = D_{AX_i}^3 * e^{-2\alpha_{AX_i} * (R_{AX_i} - R_{AX_i}^0)} + 2 * e^{-\alpha_{AX_i} * (R_{AX_i} - R_{AX_i}^0)} \quad (S28)$$

The singlet and triplet curves $E_{CX_i}^1$, $E_{CX_i}^3$, E_{OY}^1 , E_{OY}^3 are transformed smoothly, from reactants to products using the equations

$$\alpha_{CX_i} = a_{CX_i} + b_{CX_i} \frac{\tanh[c_{CX_i}(R_{AV} - R_{CX_i}^0)]}{2} \quad (S29)$$

$$\alpha_{OY} = a_{OY} + b_{OY} \frac{\tanh[c_{OY}(R_{OY} - R_{OY}^0)]}{2} \quad (S30)$$

where $D_{CX_i}^1$, $D_{CX_i}^3$, D_{OY}^1 , D_{OY}^3 , D_{OA}^1 , D_{OA}^3 , D_{CA}^1 , D_{CA}^3 , D_{AY}^1 , D_{AY}^3 , $D_{AX_i}^1$, $D_{AX_i}^3$, R_{OA}^0 , $R_{AX_i}^0$, R_{AY}^0 , R_{CA}^0 , a_{CX_i} , b_{CX_i} , c_{CX_i} , a_{OY} , b_{OY} and c_{OY} are adjustable parameters, while E_{OA}^1 , E_{OA}^3 , E_{CA}^1 , E_{CA}^3 , E_{AY}^1 , E_{AY}^3 , $E_{AX_i}^1$, $E_{AX_i}^3$ are transformed from reactants to products using the adjustable parameters α_{OA} , α_{CA} , α_{AY} and α_{AX_i} . R_{AV} is calculated for the carbon atom as

$$R_{AV} = \frac{\sum_{i=1}^3 R_{CX_i}}{3} \quad (S31)$$

The second term in Eq. (S1), V_{CO} , is represented as a simple Morse function to describe the C-O stretching motion in the C-O bond, and is given by:

$$V_{CO} = D_{CO}^1 \left[1 - e^{-a_{CO}(R_{CO} - R_{CO}^0)} \right]^2 \quad (S32)$$

This term depends on two adjustable parameters D_{CO}^1 and a_{CO} .

In order to introduce more flexibility to the functional form, the reference C- X_i , O- Y and C-O bond distances (R^0) are transformed smoothly from reactants to products using the equations

$$R_{CX_i}^0 = P_5 * R_{CX_i,R}^0 + (1 - P_5) * R_{CX_i,P}^0 \quad (S33)$$

$$R_{OY}^0 = P_5 * R_{OY,R}^0 + (1 - P_5) * R_{OY,P}^0 \quad (S34)$$

$$R_{CO}^0 = P_5 * R_{CO,R}^0 + (1 - P_5) * R_{CO,P}^0 \quad (S35)$$

where P_5 are

$$P_5 = 1 - \tanh[w_9 * (R_{AV2} - w_{10})] \quad (S36)$$

and

$$R_{AV2} = \frac{(\sum_{i=1}^3 R_{CX_i}) + R_{OY}}{4} \quad (S37)$$

$R_{CX_i,R}^0$, $R_{CX_i,P}^0$, $R_{OY,R}^0$, $R_{OY,P}^0$, $R_{CO,R}^0$, $R_{CO,P}^0$, w_9 and w_{10} are adjustable parameters, the first six $R_{X,Y}^0$ parameters associated with the equilibrium bond distances. In all, these two terms (V_{str} and V_{CO}) depend on 36 adjustable parameters.

The third term in Eq (S1), $V_{bending}$, representing the bending motions, is defined as the sum of seven harmonic potentials,

$$V_{bending} = \frac{1}{2} \sum_{i=1}^2 \sum_{j=i+1}^3 k_{XiXj}^0 k_{Xi} k_{Xj} (\theta_{XiXj} - \theta_{XiXj}^0)^2 + \frac{1}{2} \sum_{i=1}^3 k_{Xio}^0 k_{Xi} k_o (\theta_{Xio} - \theta_{Xio}^0)^2 + \frac{1}{2} k_{Yc}^0 k_Y k_C (\theta_{Yc} - \theta_{Yc}^0)^2 \quad (S38)$$

where the first term refers to the H-C-H angles, the second term to the H-C-O angles and the third term to the C-O-H angle, with the force constants given by,

$$k_{XiXj}^0 = k^{react} + k^{prod} [S_1(R_{CXi})S_1(R_{CXj}) - 1] + a_k [S_2(R_{CXk})S_2(R_{CO}) - 1] \quad (S39)$$

$$k_{Xio}^0 = k^{react} + k^{prod} [S_1(R_{CO})S_1(R_{CXi}) - 1] + a_k [S_2(R_{CXj})S_2(R_{CXk}) - 1] \quad (S40)$$

$$k_{Yc}^0 = k^{react} + k^{prod} [S_1(R_{OY})S_1(R_{CXi}) - 1] + a_k [S_2(R_{CXj})S_2(R_{CXk}) - 1] \quad (S41)$$

being

$$k^{react} = k^{prod} + a_k \quad (S42)$$

where k^{prod} and a_k are adjustable parameters, and S_1 and S_2 are switching functions,

$$S_1(R_{CXi}) = 1 - \tanh[\alpha_1(R_{CXi} - R_{CXi}^0)(R_{CXi} - \beta_1)^8] \quad (S43)$$

$$S_2(R_{CXi}) = 1 - \tanh[\alpha_2(R_{CXi} - R_{CXi}^0)(R_{CXi} - \beta_2)^8] \quad (S44)$$

$$S_1(R_{OY}) = 1 - \tanh[\alpha_3(R_{OY} - R_{OY}^0)(R_{OY} - \beta_3)^8] \quad (S45)$$

$$S_2(R_{OY}) = 1 - \tanh[\alpha_4(R_{OY} - R_{OY}^0)(R_{OY} - \beta_4)^8] \quad (S46)$$

$$S_1(R_{CO}) = 1 \quad (S47)$$

$$S_2(R_{CO}) = 1 \quad (S48)$$

where $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \beta_1, \beta_2, \beta_3$ and β_4 are adjustable parameters. $S_1(R_{CO})$ and $S_2(R_{CO})$ are fixed to 1 because the C-O bond is not broken in this hydrogen abstraction reaction.

The force constants k_{xi}, k_Y, k_O and k_C are defined as a function of the distances R_{ab} in the following forms,

$$k_{xi} = A_1 \exp[-A_2(R_{CXi} - R_{CXi}^0)^2] \quad (S49)$$

$$A_1 = 1 - \exp[-aa_1(R_{AXi})^2] \quad (S50)$$

$$A_2 = aa_2 + aa_3 \exp[-aa_4(R_{AXi} - R_{AXi}^0)^2] \quad (S51)$$

$$k_Y = A_3 \exp[-A_4(R_{OY} - R_{OY}^0)^2] \quad (S52)$$

$$A_3 = 1 - \exp[-aa_5(R_{AY})^2] \quad (S53)$$

$$A_4 = aa_6 + aa_7 \exp[-aa_8(R_{AY} - R_{AY}^0)^2] \quad (S54)$$

$$k_O = k_C = A_5 \exp[-A_6(R_{CO} - R_{CO}^0)^2] \quad (S55)$$

In these terms, $aa_1, aa_2, aa_3, aa_4, aa_5, aa_6, aa_7, aa_8, A_5$ and A_6 are adjustable parameters.

With respect to the reference angles, in this system we have three different reference angles, H-C-H, H-C-O and finally C-O-H. They are also allowed to relax from reactant ($\tau_{XX} = 108.6^\circ, \tau_{XO} = 111.9^\circ$ and $\tau_{YC} = 108.0^\circ$) to the product configurations,

$$\begin{aligned} \theta_{xiXj}^0 &= \tau_{XX} + (\tau_{XX} - \pi/2)[S_\varphi(R_{CXi})S_\varphi(R_{CXj}) - 1] \\ &\quad + (\tau_{XX} - 2\pi/3)[S_\theta(R_{CXk})S_\theta(R_{CO}) - 1] \end{aligned} \quad (S56)$$

$$\begin{aligned} \theta_{xiO}^0 &= \tau_{XO} + (\tau_{XO} - \pi/2)[S_\varphi(R_{CO})S_\varphi(R_{CXi}) - 1] \\ &\quad + (\tau_{XO} - 2\pi/3)[S_\theta(R_{CXj})S_\theta(R_{CXk}) - 1] \end{aligned} \quad (S57)$$

$$\theta_{YC}^0 = \tau_{YC} + (\tau_{YC} - \pi/2)[S_\varphi(R_{CO})S_\varphi(R_{OY}) - 1] \quad (S58)$$

using the following switching functions,

$$S_\varphi(R_{CXi}) = 1 - \tanh \left\{ A_{\varphi 1} (R_{CXi} - R_{CXi}^0) \exp[B_{\varphi 1} (R_{CXi} - C_{\varphi 1})]^3 \right\} \quad (S59)$$

$$S_\varphi(R_{OY}) = 1 - \tanh \left\{ A_{\varphi 2} (R_{OY} - R_{OY}^0) \exp[B_{\varphi 2} (R_{OY} - C_{\varphi 2})]^3 \right\} \quad (S60)$$

$$S_{\varphi}(R_{CO}) = 1 - \tanh\left\{A_{\varphi}(R_{CO} - R_{CO}^0)\exp[B_{\varphi}(R_{CO} - C_{\varphi})]^3\right\} \quad (S61)$$

$$S_{\theta}(R_{CXi}) = 1 - \tanh\{A_{\theta 1}(R_{CXi} - R_{CXi}^0)\exp[B_{\theta 1}(R_{CXi} - C_{\theta 1})]^3\} \quad (S62)$$

$$S_{\theta}(R_{CO}) = 1 - \tanh\{A_{\theta}(R_{CO} - R_{CO}^0)\exp[B_{\theta}(R_{CO} - C_{\theta})]^3\} \quad (S63)$$

where $A_{\varphi 1}$, $B_{\varphi 1}$, $C_{\varphi 1}$, $A_{\varphi 2}$, $B_{\varphi 2}$, $C_{\varphi 2}$, A_{φ} , B_{φ} , C_{φ} , $A_{\theta 1}$, $B_{\theta 1}$, $C_{\theta 1}$, A_{θ} , B_{θ} and C_{θ} are adjustable parameters. In total, the $V_{bending}$ potential needs 35 parameters to be fitted in the calibration process.

The next term in Eq. (S1), V_{op} , represents a quadratic-quartic potential whose aim is to describe correctly the out-of-plan motion of the CH_2O group in the CH_2OH radical.

$$V_{op} = \sum_{i=1}^3 f_{\Delta}^{CXi} \sum_{j \neq i}^3 (\Delta_{ij})^2 + \sum_{i=1}^3 h_{\Delta}^{CXi} \sum_{j \neq i}^3 (\Delta_{ij})^4 \quad (S64)$$

The force constants, f_{Δ} and h_{Δ} , are allowed to relax from the reactant, where the CH_2O group in the CH_3OH molecule shows a pyramidal structure, to products, where the CH_2O group in the CH_2OH radical shows quasi-planar geometry. We use the following S_3 switching function,

$$f_{\Delta}^{CXi} = [1 - S_3(R_{CXi})]S_3(R_{CXj})S_3(R_{CXk})S_3(R_{CO})f_{\Delta}^{prod} \quad (S65)$$

$$h_{\Delta}^{CXi} = [1 - S_3(R_{CXi})]S_3(R_{CXj})S_3(R_{CXk})S_3(R_{CO})h_{\Delta}^{prod} \quad (S66)$$

$$S_3(R_{CXi}) = 1 - \tanh[\alpha_{3s}(R_{CXi} - R_{CXi}^0)(R_{CXi} - \beta_{3s})^2] \quad (S67)$$

$$S_3(R_{CO}) = 1 \quad (S68)$$

The angle measuring the deviation from the reference angle is,

$$\Delta_{ij} = \arccos\left(\frac{(\vec{q}_k - \vec{q}_j) \times (\vec{q}_l - \vec{q}_j)}{\|(\vec{q}_k - \vec{q}_j) \times (\vec{q}_l - \vec{q}_j)\|} \cdot \frac{\vec{r}_i}{\|\vec{r}_i\|}\right) - \theta_{ij}^0 \quad (S69)$$

with $(\vec{q}_k - \vec{q}_j)$ and $(\vec{q}_l - \vec{q}_j)$ being two vectors between three of the atoms bonded to the carbon atom and r_i the vector between the carbon and each of the atoms directly bonded to it. Therefore, the first term to the right of (S69) represents the angle between the CX_i bond and a vector perpendicular to the plane described by the three other atoms bonded to the carbon. The reference angle θ_{ij}^0 , is defined in Eq. (S56).

The V_{op} potential needs 4 parameters (α_{3s} , β_{3s} , f_{Δ}^{prod} and h_{Δ}^{prod}) to be fitted in the calibration process.

Finally, to include the torsion motion about the C-O bond, we include a torsional term, V_{tor} in Eq. S1, given as a cosine function of the torsional angle γ ,

$$V_{tor} = \sum_{i=1}^3 \frac{V_3}{3} [1 + \cos(3\gamma_{X_iCOY})] t_1(i) t_2 \quad (S70)$$

being,

$$t_1(i) = \frac{1}{2} [1 - \tanh(w_1(R_{CX_i} - w_2))] \quad (S71)$$

$$t_2 = \frac{1}{2} [1 - \tanh(w_7(R_{OY} - w_8))] \quad (S72)$$

This term depends on 5 adjustable parameters (V_3 , w_1 , w_2 , w_7 , and w_8), where V_3 is associated with the torsional barrier height.

In total, the new potential for the H+CH₃OH reaction, which proceeds by two channels, depends on 80 adjustable parameters, this being the major challenge for our group in the development of potential energy surfaces in polyatomic systems. The 80 parameters appear in Table S1. Note that this surface is symmetric with respect to the permutation of the 3 H atoms in the CH₃ group in methanol and that the 80 parameters give great flexibility to the potential form.

b) Fitting process

The second step in the development of the PES is the fitting of the 80 parameters to high-level *ab initio* calculations. It is a tedious process (and similar in time to the development of the analytical form). Different strategies have been tested in our group; as a first approximation to the problem is the case of the least-square approach

$$R = \sum_x |E(x) - V(x, p)|^2 \quad (S73)$$

$E(x)$ and $V(x, p)$, being, respectively, the *ab initio* inputs at each point (x) used as input in the analytical VB-MM function, Eq. (S1), depending on the 80 parameters (p). However, as previously noted (see for instance Refs. 17 and 23) this approach is unsuccessful when all parameters are simultaneously introduced. So, we use an

alternative divide-and conquer approach, which is an iterative process. Since this method has been previously described in detail (Refs. 17 and 23), here we present only a brief summary to avoid unnecessary repetition. In the first step, the properties of reactants and products (geometry, vibrational frequencies and energy) are fitted to the input data, involving the following parameters: $R_{CX_i,R}^0, R_{CX_i,P}^0, D_{CX_i}^1, D_{CX_i}^3, a_{CX_i}, b_{CX_i}, c_{CX_i}, R_{OY,R}^0, R_{OY,p}^0, D_{OY}^1, D_{OY}^3, a_{OY}, b_{OY}, c_{OY}, R_{CO,R}^0, R_{CO,P}^0, w_9, w_{10}, D_{CO}^1, \alpha_{CO}, R_{AX_i}^0, D_{AX_i}^1, D_{AX_i}^3, \alpha_{AX_i}, R_{AY}^0, D_{AY}^1, D_{AY}^3$ and α_{AY} . In the second step, we focus attention on the description of the saddle point (barrier height and imaginary vibrational frequency, which describes the topology in this zone and the fall to the reactant and product asymptotes). The following parameters are used in this step: $R_{CA}^0, D_{CA}^1, D_{CA}^3, \alpha_{CA}, R_{OA}^0, D_{OA}^1, D_{OA}^3$ and α_{OA} . Finally, in the third step the reaction path or minimum energy path (MEP), and the reaction valley are fitted to the *ab initio* input information [where 90 points were calculated describing the MEP (energy, gradient and Hessian)]. Note that since in the CCSD(T) level the second derivatives of the energy are numerical, the *ab initio* Hessian calculations are computationally very expensive: with 7 atoms we have 21 coordinates and 441 (21x21) energy calculations per point. In total this represents about 40,000 energy calculations, taking into account the 90 points on the MEP. To relax the reactive system from reactants to products and to obtain a continuous and smooth potential, in the last two steps we used the parameters related with the switching functions, Eqs. (S43-S63, S67-68, S71-72).

As previously noted, this three-step process is iterative, and is repeated until convergence with the *ab initio* input data. Obviously, this represents a tedious task and is very time-consuming. Once the fitting process was concluded, we obtained the final set of 80 parameters defining the new PES-2022 surface. Table S1 lists the best set of parameters. Figure S1 is a diagram representation of the fitting process, while Figure S2 plots 2D representations of the new PES-2022 surface, for both channels. Finally, note that the new PES-2022 can be obtained upon request from the authors, prior its publication in POTLIB library (Ref. 24)

Table S1. Final fitting parameters for the PES-2022 surface describing the H + CH₃OH → H₂ + CH₂OH/CH₃O gas-phase reactions.

Parameter	Value
$V_{str} + V_{CO}$	36
parameters	
$R_{CX_i,R}^0$	1.09047 Å
$R_{CX_i,P}^0$	1.08177 Å
$D_{CX_i}^1$	106.23000 kcal mol ⁻¹
$D_{CX_i}^3$	38.00400 kcal mol ⁻¹
a_{CX_i}	1.50300 Å ⁻¹
b_{CX_i}	0.52500 Å ⁻¹
c_{CX_i}	0.51404 Å ⁻¹
$R_{OY,R}^0$	0.95897 Å
$R_{OY,p}^0$	0.96077 Å
D_{OY}^1	117.23000 kcal mol ⁻¹
D_{OY}^3	44.00400 kcal mol ⁻¹
a_{OY}	1.95300 Å ⁻¹
b_{OY}	0.42500 Å ⁻¹
c_{OY}	0.51404 Å ⁻¹
$R_{CO,R}^0$	1.42007 Å
$R_{CO,P}^0$	1.37500 Å
w_9	1.5000d0
w_{10}	1.08507d0
D_{CO}^1	109.94900 kcal mol ⁻¹
α_{CO}	1.934 Å ⁻¹
$R_{AX_i}^0$	0.77191 Å
$D_{AX_i}^1$	114.458 kcal mol ⁻¹
$D_{AX_i}^3$	22.064 kcal mol ⁻¹
α_{AX_i}	1.9557 Å ⁻¹
R_{AY}^0	0.77191 Å
D_{AY}^1	114.458 kcal mol ⁻¹

D_{AY}^3	22.064 kcal mol ⁻¹
α_{AY}	1.9557 Å ⁻¹
R_{CA}^0	1.39897 Å
D_{CA}^1	39.009 kcal mol ⁻¹
D_{CA}^3	37.000 kcal mol ⁻¹
α_{CA}	2.0890285 Å ⁻¹
R_{OA}^0	1.60897 Å
D_{OA}^1	29.609 kcal mol ⁻¹
D_{OA}^3	23.400 kcal mol ⁻¹
α_{OA}	2.0170285 Å ⁻¹
<hr/>	
$V_{bending}$	34
parameters	
<hr/>	
A_φ	0.528790d0 Å ⁻¹
B_φ	1.200664d0 Å ⁻³
C_φ	1.420074d0 Å
$A_{\varphi 1}$	0.19700d0 Å ⁻¹
$B_{\varphi 1}$	1.20600d0 Å ⁻³
$C_{\varphi 1}$	1.08200d0 Å
$A_{\varphi 2}$	0.19700d0 Å ⁻¹
$B_{\varphi 2}$	1.20600d0 Å ⁻³
$C_{\varphi 2}$	0.96800d0 Å
$A_{\theta 1}$	1.65781d0 Å ⁻¹
$B_{\theta 1}$	0.950600d0 Å ⁻³
$C_{\theta 1}$	1.08201d0 Å
A_θ	1.45781d0 Å ⁻¹
B_θ	0.950600d0 Å ⁻³
C_θ	1.42001d0 Å
aa_1	0.49001d0 Å ⁻²
aa_2	1.59995d0 Å ⁻²
aa_3	2.16996d0 Å ⁻²
aa_4	11.56595d0 Å ⁻²
aa_5	0.05001d0 Å ⁻²

aa_6	1.30095d0 \AA^{-2}
aa_7	1.49996d0 \AA^{-2}
aa_8	11.46595d0 \AA^{-2}
A_5	1.20997d0 \AA^{-2}
A_6	1.949d0 \AA^{-2}
α_1	1.53137d0 \AA^{-1}
β_1	1.09463d0 \AA
α_3	1.01474d0 \AA^{-1}
β_3	0.96898d0 \AA
α_2	1.53137d0 \AA^{-1}
β_2	1.09463d0 \AA
α_4	1.51474d0 \AA^{-1}
β_4	0.96898d0 \AA
k^{prod}	0.44770d0 mdyne \AA rad^{-2}
a_k	0.12600d0 mdyne \AA rad^{-2}
<hr/>	
V_{op} parameters	4
<hr/>	
α_{3s}	0.12770d0 \AA^{-1}
β_{3s}	1.08200d0 \AA
f_{Δ}^{prod}	0.19770d0 \AA rad^{-2}
h_{Δ}^{prod}	0.09600d0 \AA rad^{-4}
<hr/>	
V_{tor} parameters	5
<hr/>	
V_3	0.03000 kcal mol $^{-1}$
w_1	0.11000 \AA^{-1}
w_2	1.08697 \AA
w_7	0.11000 \AA^{-1}
w_8	1.08367 \AA
<hr/>	

Figure S1. Diagram representation of the fitting process.

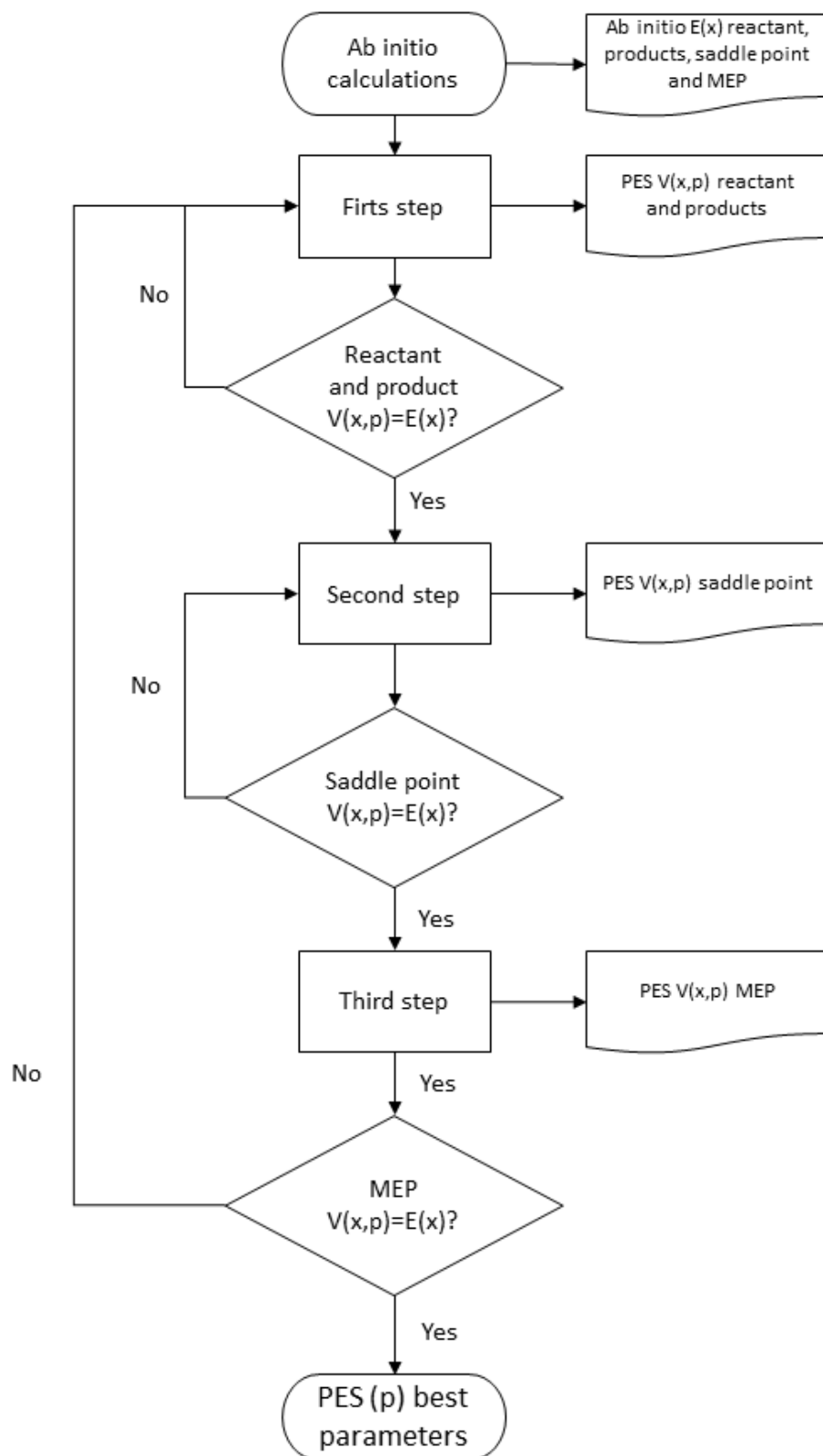
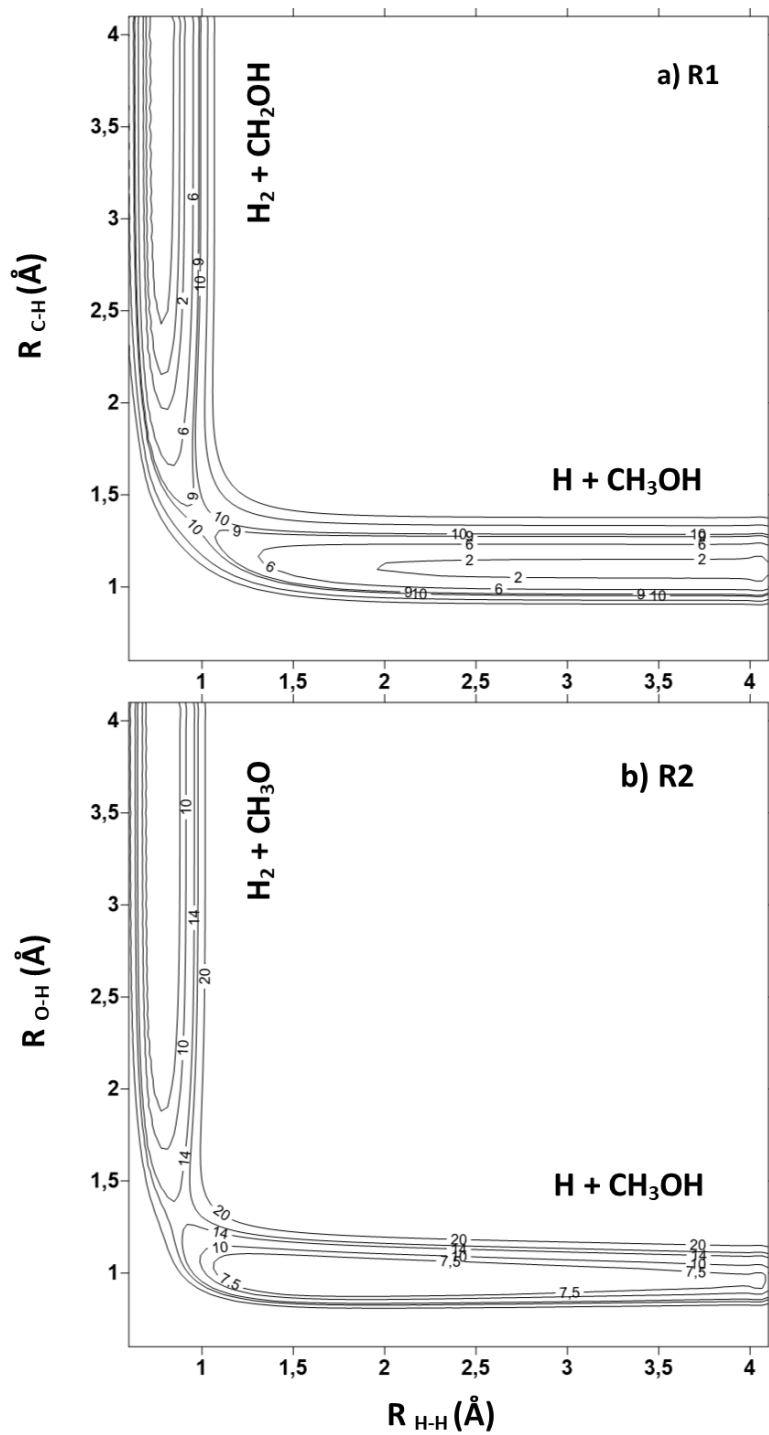


Figure S2. Plots 2D representations of the new PES-2022 surface, for both channels. Distances in Å and energy in kcal mol⁻¹.



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