**Supplementary Information**

# Title: Rate constant calculations of the $GeH_4$ + OH/OD → $GeH_3$ + $H_2O$/HOD reactions using an ab initio based full-dimensional potential energy surface

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## ANALYTICAL FUNCTIONAL FORM AND FITTING PROCEDURE

### a) Analytical potential

The new analytical PES function describing the $GeH_4 + OH \rightarrow GeH_3 + H_2O$ system is based on our surface for the similar $CH_4$ + OH hydrogen abstraction reaction,[22] which is basically a valence bond-molecular mechanics (VB-MM) potential energy surface. We shall start by presenting mathematical details and terms included.

The potential energy for a given geometry, $V$, is given by the sum of four terms:

$$V = V_{\mathrm{stretch}} + V_{val} + V_{\mathrm{op}} + V_{water} \ , \tag{S1}$$

The first term represents a stretching potential defined as the sum of four London-Eyring-Polanyi (LEP) terms,

$$V_{\mathrm{stretch}} = \sum_{i=1}^{4} V_3\left(R_{\mathrm{GeH_i}}, R_{\mathrm{GeO}}, R_{\mathrm{H_iO}}\right) , \tag{S2}$$

where $H_i$ stands for one of the four germane hydrogens, O is the attacking oxygen atom and $R$ is the distance between the two subscript atoms. For the sake of completeness the $V_3$ potential is,

$$\begin{aligned} V_3(R_{\mathrm{GeH_i}}, R_{\mathrm{GeO}}, R_{\mathrm{H_iO}}) &= Q(R_{\mathrm{GeH_i}}) + Q(R_{\mathrm{GeO}}) + Q(R_{\mathrm{H_iO}}) - \\ &- \sqrt{\frac{1}{2}\left[J(R_{\mathrm{GeH_i}}) - J(R_{\mathrm{H_iO}})\right]^2 + \frac{1}{2}\left[J(R_{\mathrm{H_iO}}) - J(R_{\mathrm{GeO}})\right]^2 + \frac{1}{2}\left[J(R_{\mathrm{GeO}}) - J(R_{\mathrm{GeH_i}})\right]^2} \ , \end{aligned} \tag{S3}$$

$$Q(R_{XY}) = \frac{E^1(R_{XY}) + E^3(R_{XY})}{2} \ , \tag{S4}$$

$$J(R_{XY}) = \frac{E^1(R_{XY}) - E^3(R_{XY})}{2} \ , \tag{S5}$$

$$E^1(R_{XY}) = D^1_{XY}\left\{\exp\left(-2\alpha_{XY}\left[R_{XY} - R^e_{XY}\right]\right) - 2\exp\left(-\alpha_{XY}\left[R_{XY} - R^e_{XY}\right]\right)\right\} , \tag{S6}$$

$$E^3(R_{XY}) = D^3_{XY}\left\{\exp\left(-2\alpha_{XY}\left[R_{XY} - R^e_{XY}\right]\right) + 2\exp\left(-\alpha_{XY}\left[R_{XY} - R^e_{XY}\right]\right)\right\} , \tag{S7}$$

which includes 14 fitting parameters: the triplet and singlet dissociation energies, $D^3_{XY}$ and $D^1_{XY}$, the equilibrium bond distances, $R^e_{XY}$, and the Morse parameters, $\alpha_{XY}$. To introduce more flexibility, the $\alpha_{\mathrm{GeH}}$ parameter is a function of the Ge-H distance

$$\alpha_{\mathrm{GeH}} = a_{\mathrm{GeH}} + b_{\mathrm{GeH}}\left(\frac{\tanh\left[c_{\mathrm{GeH}}\left(\bar{R} - R^e_{\mathrm{GeH}}\right)\right] + 1}{2}\right), \tag{S8}$$

$\bar{R}$ being the average of the four $R_{\mathrm{GeH}_i}$ distances,

$$\bar{R} = \frac{1}{4}\sum_{i=1}^{4} R_{\mathrm{GeH}_i} , \tag{S9}$$

With this modification, $\alpha_{\mathrm{GeH}}$ changes smoothly along the reaction path from its value at germane to its value at the $\mathrm{GeH}_3$ radical.

The second term, $V_{\mathrm{val}}$, representing the harmonic potential is defined as the sum of six harmonic potentials,

$$V_{\mathrm{val}} = \frac{1}{2}\sum_{i=1}^{3}\sum_{j=i+1}^{4} k^0_{ij} k_i k_j \left(\theta_{ij} - \theta^0_{ij}\right)^2 , \tag{S10}$$

where $\theta^0_{ij}$ are reference angles and $k^0_{ij}$ and $k_i$ are force constants. The $k^0_{ij}$ terms are allowed to relax from reactants to products, where $k^{\mathrm{GeH}_3}$, $a_k$ and $b_k$ are fitting parameters,

$$\begin{aligned} k^0_{ij} = k^{\mathrm{GeH}_3} &+ a_k \exp\left[-b_k (R_{GeHi} - R^e_{GeH})^2\right] \exp\left[-b_k (R_{GeHj} - R^e_{GeH})^2\right] \\ &\exp\left[-b_k (R_{GeHk} - R^e_{GeH})^2\right] \exp\left[-b_k (R_{GeHl} - R^e_{GeH})^2\right] \end{aligned}, \tag{S11}$$

The constant force $k_i$ is defined as a function of both the $R_{\mathrm{GeH_i}}$ and $R_{\mathrm{H_iO}}$ distances,

$$k_i = A_1 \exp\left[-A_2\left(R_{\mathrm{GeH_i}} - R^e_{\mathrm{GeH}}\right)^2\right], \tag{S12}$$

$$A_1 = 1 - \exp\left[-aa_1\left(R_{\mathrm{H_iO}}\right)^2\right], \tag{S13}$$

$$A_2 = aa_2 + aa_3 \exp\left[-aa_4\left(R_{\mathrm{H_iO}} - R^e_{\mathrm{H_iO}}\right)^2\right], \tag{S14}$$

where four new adjustable parameters are included, namely $aa_i$.

With respect to the reference angles, they are also allowed to relax from germane, τ = 109.47°, to the $\mathrm{GeH}_3$ radical, $\tau_{\mathrm{GeH}}$ = 122.0°,

$$\begin{aligned}\vartheta_{ij}^{o} &= \tau + (\tau - \tau_{GeH})\left[S_{\rho}(R_{GeHi}) - S_{\rho}(R_{GeHj}) - 1\right] \\ &+ (\tau - 2\pi/3)\left[S_{\theta}(R_{GeHi}) - S_{\theta}(R_{GeHj}) - 1\right]\end{aligned} , \tag{S15}$$

using the following switching functions,

$$S_{\varphi}\left(R_{\mathrm{GeH_i}}\right) = 1 - \tanh\left\{A_{\varphi}\left(R_{\mathrm{GeH_i}} - R^{e}_{\mathrm{GeH}}\right)\exp\left[B_{\varphi}\left(R_{\mathrm{GeH_i}} - C_{\varphi}\right)^{3}\right]\right\} , \tag{S16}$$

$$S_{\theta}\left(R_{\mathrm{GeH_i}}\right) = 1 - \tanh\left\{A_{\theta}\left(R_{\mathrm{GeH_i}} - R^{e}_{\mathrm{GeH}}\right)\exp\left[B_{\theta}\left(R_{\mathrm{GeH_i}} - C_{\theta}\right)^{3}\right]\right\} , \tag{S17}$$

In total, the $V_{\mathrm{val}}$ potential needs 13 terms to be fitted in the calibration process.

The third term, $V_{\mathrm{op}}$, represents a quadratic-quartic potential

$$V_{\mathrm{op}} = \sum_{i=1}^{4} f_{\Delta_i} \sum_{\substack{j=1 \\ j\neq i}}^{4} \left(\Delta_{ij}\right)^{2} + \sum_{i=1}^{4} h_{\Delta_i} \sum_{\substack{j=1 \\ j\neq i}}^{4} \left(\Delta_{ij}\right)^{4} , \tag{S18}$$

whose aim is to correctly describe the out-of-plane motion of GeH$_3$ radical in the products. The force constants, $f_{\Delta_i}$ and $h_{\Delta_i}$, are allowed to relax from reactants, where the GeH$_3$ fragment shows a pyramidal structure, to products, where it shows a quasi-planar geometry, by means of the S$_3$ switching function,

$$f_{\Delta_i} = \left[1 - S_3\left(R_{\mathrm{GeH_i}}\right)\right] f_{\Delta}^{\mathrm{GeH_3}} , \tag{S19}$$

$$h_{\Delta_i} = \left[1 - S_3\left(R_{\mathrm{GeH_i}}\right)\right] h_{\Delta}^{\mathrm{GeH_3}} , \tag{S20}$$

$$S_3\left(R_{\mathrm{GeH_i}}\right) = 1 - \tanh\left[\alpha_3^{s}\left(R_{\mathrm{GeH_i}} - R^{e}_{\mathrm{GeH}}\right)\left(R_{\mathrm{GeH_i}} - \beta_3^{s}\right)^{2}\right] , \tag{S21}$$

where $f_{\Delta}^{\mathrm{GeH_3}}$, $h_{\Delta}^{\mathrm{GeH_3}}$, $\alpha_3^{s}$, and $\beta_3^{s}$ are fitting parameters. The angle measuring the deviation from the reference angle is,

$$\Delta_{ij} = \mathrm{acos}\left(\frac{\left(\vec{r}_k - \vec{r}_j\right)\times\left(\vec{r}_l - \vec{r}_j\right)}{\left\|\left(\vec{r}_k - \vec{r}_j\right)\times\left(\vec{r}_l - \vec{r}_j\right)\right\|}\frac{\vec{r}_i}{\left\|\vec{r}_i\right\|}\right) - \theta_{ij}^{0} , \tag{S22}$$

with $\vec{r}_i$, $\vec{r}_j$, $\vec{r}_k$, and $\vec{r}_l$ being the vectors going from the Ge atom to the i, j, k, and l hydrogen atoms, respectively. The reference angles, $\theta_{ij}^{0}$, are defined in Eq. (S15).

Finally, the water product formed in the reaction is defined by the sum of two terms: i) a Morse function describing the O–H$_j$ bond ($V_M$)

$$V_M = D^{1}{}_{OH}\left\{1 - \exp\left[-\alpha_{OH}(R_{OHj} - R^{e}_{OH})\right]\right\}^{2} \tag{S23}$$

where $D^1_{OH}$, $R^e_{OH}$ and $\alpha_{OH}$ are, respectively, the OH dissociation energy, the OH equilibrium bond length (0.971 Å), and the Morse parameter to correctly describe the OH radical vibrational frequency; and ii) a harmonic bending term ($V_{\mathrm{harm}}$) describing the HOH bending mode,

$$V_{harm} = \frac{1}{2}\sum_{i=1}^{4} K_i(\rho_i - \rho_i^o)^2 \tag{S24}$$

where $\rho_i^o$ is the HOH equilibrium angle (104.7132°), and the summation was extended to the four hydrogen atoms of germane to maintain the PES symmetric with respect to the permutation of these four atoms. To include more flexibility in the function and provide the correct asymptotic values, the force constant, $K_i$, was allowed to relax using the switching function,

$$K_i = K_a^o\left\{1 - \tanh\left[\varepsilon_{OH}(R_{OHj} - R^e_{OH})\right]\right\} \tag{S25}$$

where $K_a^o$ and $\varepsilon_{OH}$ are parameters fitted to reproduce the value of the water vibrational frequencies along the reaction path. Thus, the $V_{\mathrm{water}}$ function includes 3 parameters in the calibration process.

The new PES, therefore, depends on 34 parameters, 14, 13, 4 and 3, respectively, to describe the stretching, the valence term, the out-of-plane potential and the water function. These 34 parameters give great flexibility to the functional form, and in addition the VB-MM functional form remains physically intuitive. Note that this surface is symmetric with respect to the permutation of the four hydrogens in germane, and it provides not only the energy of the reactive process but also the analytical first energy derivatives, i.e., the gradients, which represents a computational advantage in kinetics and quasi-classical dynamics calculations.

### b) Fitting procedure.

With the functional form previously described and using as input information all the stationary points and the reaction path at the ab initio level, the 34 parameters were fitted. Following our recent works on PESs in polyatomic systems,[23-25] in the fitting procedure there are two sequential steps, the first being manual and the second automated. In the first one, given that the parameters in the VB-MM potential are directly related to physical and chemical properties by construction (geometries, vibrational frequencies, exothermicity or barrier height) we attempted manually to fit the parameters to reproduce these properties. This is a process in steps, laborious and difficult because the parameters are not independent, and usually refitting of the previously fitted parameters is needed. In the first approach, using the $R^e_{\mathrm{GeH_i}}$, $R^e_{\mathrm{GeO}}$, $R^e_{\mathrm{H_iO}}$, $D^1_{\mathrm{GeH_i}}$, $D^1_{\mathrm{H_iO}}$, $\alpha_{\mathrm{H_iO}}$, $f_\Delta^{\mathrm{GeH3}}$, $h_\Delta^{\mathrm{GeH3}}$, $k^{\mathrm{GeH_3}}$, $a_k$, $b_k$, , $R^e_{OH}$, and $\varepsilon_{\mathrm{OH}}$ parameters, we attempted to reproduce the geometries, vibrational frequencies and classical reaction energy of reactants and products at the reference ab initio CCSD(T)/cc-pVTZ level. In the second approach, we aimed to reproduce the saddle point properties (geometry, vibrational frequencies, with special attention to the imaginary value, and the barrier height, which is very important in kinetics calculations) at the same ab initio level using the six $D^3_{\mathrm{GeH_i}}$, $D^3_{\mathrm{H_iO}}$, $D^1_{\mathrm{GeO}}$, $D^3_{\mathrm{GeO}}$, $\alpha_{\mathrm{GeO}}$, and $c_{\mathrm{GeH}}$ parameters. In the third approach we fit the parameters of the switching functions which describe changes along the reaction path, $A_1$, $A_2$, (S14), $S_\theta$, $S_\phi$, (S16,S17) and $S_3$ (S21). Thus, the parameters $aa_1$, $aa_2$, $aa_3$, $aa_4$, $\alpha_1^s$, $\alpha_2^s$, $\alpha_3^s$, $\beta_3^s$, $A_\theta$, $B_\theta$, $C_\theta$, $A_\phi$, $B_\phi$, and $C_\phi$ were obtained. Note that these steps led to a first set of parameters which were used as the starting point for a new manual refit. This process was repeated until a reasonable convergence with the values of the reference ab initio level was obtained for all the analyzed properties.

When one considers that the fitted parameters reasonably reproduce the main topological characteristics of the reactive system, from reactants to products, an automated procedure is used. However, it is well known that to find a global minimum for the fit is very hard, and to make matters worse, the final result is dependent on the initial parameters; one usually obtains a number of distinct sets of initial parameters, which are equally probable and good. This represents a serious limitation of the procedure. Therefore we have developed an automated multi-beginning least-squares procedure,[23] (local optimization method), which gives the parameters that minimize (locally) the function

$$R = \sum_x \left| E(x) - F(x,p) \right|^2 , \tag{S26}$$

where for a set of coordinates of the atoms, {x}; $E(x)$ and $F(x, p)$ represent the potential energy and the analytical function depending on the parameters, {p}, respectively. To solve the limitations of the global fitting, at least in part, we adopted the following approach, which takes into account the first and second derivatives of the energy, gradient $g(x)$ and Hessian $H(x)$, and a set of weights, $w_x^e$, $w_x^g$, and $w_x^H$,

$$R = \sum_x w_x^e \left| E(x) - F(x,p) \right|^2 + \sum_x w_x^g \left| g(x) - \frac{\partial F(x,p)}{\partial x} \right|^2 + \\ + \sum_x w_x^H \left| H(x) - \frac{\partial^2 F(x,p)}{\partial x^2} \right|^2 \tag{S27}$$

This algorithm begins with the Powell's method for local optimization, and then applies a multi-beginning method to search for a global optimum. The choice of the weights is critical in the minimization process. Thus, for instance, if we focus on the description of the transition state region, we will give higher weights to the imaginary vibrational frequency and to points near the saddle point. As gradients and Hessians are included in the fitting procedure, this information must be provided as input data at the ab initio level. Thus, the gradients and Hessians for 50 points along the minimum energy path were computed at the CCSD(T)/cc-pVTZ level. At this level the vibrational frequencies were numerically calculated, and to compute a Cartesian coordinate Hessian approximately 441 energies (441 is 21 squared, and 21 is 3 coordinates per atom times 7 atoms) were necessary. As 50 points were considered along the path, 22050 (441 times 50) energy points were calculated, which were used in the fitting process.

Once both steps, manual and automated, were finished, we took the present values of the 35 parameters as the best set of this fitting algorithm. These values are listed in Table S1 and a 3D representation of the new PES is plotted in Figure S1. As has been clearly shown in this Supplementary Information, the minimization process is not a trivial task; it is time consuming and the final set of parameters, despite reproducing the reference ab initio data used as input information, is not unique. Finally, as noted in the present paper, the new potential energy surface can be obtained upon request from the authors, prior to its publication in the POTLIB library.[27]

**Table S1**. Final fitting parameters for the PES-2015 surface.

| Parameter | Value |
|---|---|
| $R^{e}_{GeH}$ | 1.52500 Å |
| $D^{1}_{GeH}$ | 86.50000 kcal mol$^{-1}$ |
| $D^{3}_{GeH}$ | 41.50000 kcal mol$^{-1}$ |
| $a_{GeH}$ | 1.43925 Å$^{-1}$ |
| $b_{GeH}$ | 0.12330 Å$^{-1}$ |
| $c_{GeH}$ | 2.00400 Å$^{-1}$ |
| $R^{e}_{HO}$ | 0.97060 Å |
| $D^{1}_{HO}$ | 120.94800 kcal mol$^{-1}$ |
| $D^{3}_{HO}$ | 31.86417 kcal mol$^{-1}$ |
| $\alpha_{HO}$ | 2.18200 Å$^{-1}$ |
| $R^{e}_{GeO}$ | 1.90035 Å |
| $D^{1}_{GeO}$ | 41.50283 kcal mol$^{-1}$ |
| $D^{3}_{GeO}$ | 10.50589 kcal mol$^{-1}$ |
| $\alpha_{GeO}$ | 0.67621 Å$^{-1}$ |
| $\alpha^{s}_{3}$ | 0.2019100 Å$^{-1}$ |
| $\beta^{s}_{3}$ | -0.6068400 Å$^{-1}$ |
| $A_{\varphi}$ | 0.5287900 Å$^{-1}$ |
| $B_{\varphi}$ | 0.4006600 Å$^{-3}$ |
| $C_{\varphi}$ | 11.8809900 Å |
| $A_{\theta}$ | 0.9078700 Å$^{-1}$ |
| $B_{\theta}$ | 0.3548900 Å$^{-3}$ |
| $C_{\theta}$ | 1.8915500 Å |
| $f_{\Delta}^{GeH3}$ | 0.0150000 mdyne Å rad$^{-2}$ |
| $h_{\Delta}^{GeH3}$ | 0.1915000 mdyne Å rad$^{-4}$ |
| $k^{GeH3}$ | 0.3060000 mdyne Å rad$^{-2}$ |
| $a_{k}$ | 0.1260000 mdyne Å rad$^{-2}$ |
| $b_{k}$ | 50.7132 Å$^{-2}$ |
| $aa_{1}$ | 0.173746 Å$^{-2}$ |
| $aa_{2}$ | 1.599960 Å$^{-2}$ |
| $aa_{3}$ | 2.166595 Å$^{-2}$ |
| $aa_{4}$ | 11.569980 Å$^{-2}$ |
| $K^{o}_{a}$ | 0.7300000 mdyne Å rad$^{-2}$ |
| $\varepsilon_{OH}$ | 1.1080000 Å$^{-1}$ |
| $\rho^{o}$ | 104.7132000 degrees |

**Figure S1**. 3D representation of the PES-2015 surface. Distances in Å and energies in kcal mol$^{-1}$.