Comment on "Anisotropy of Shear-Induced Mechanochemical Reaction Rates of Surface Adsorbates; Implications for Theoretical Models" by R. Rana, G. D. Kenmoe, F. Sidoroff, R. Bavisotto, N. Hopper, and W. T. Tysoe, The Journal of Physical Chemistry C, 2022, 126, 11585-11593

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Abstract

The definition of a reaction path is central in mechanochemistry. It provides a one-dimensional description of a molecular rearrangement in an $N-$dimensional configuration space. One can apply mechanical stress in a defined direction to the molecule. We contradict the commented

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paper that the curve of force displayed stationary points (FDSP) under mechanical stress is the steepest descent of the original potential energy surface. We propose a different explanation for the observed dissociation of surface adsorbates, in contrast to the commented paper.

1 Introduction

First, we would like to congratulate the authors on their effort to analyze shear-induced mechano-chemical reaction rates of surface adsorbate atoms.[1] These experimental results are very exciting. The study provides real-world data of an experiment, however, the paper has some important inconsistencies both in the model and in the numeric part. The incorrect theoretical part prevents definitive conclusions from the analysis.

The potential energy surface (PES) and the reaction path (RP) are basic concepts of many mechanochemistry models. The RP is a one-dimensional description of a chemical reaction through a sequence of molecular geometries in an N-dimensional configuration space. Using the RP means that only geometric properties of the PES are taken into account. Note that no dynamic information can be sought from these pathways when a reaction is analyzed by this model. The most widely used curve to represent an RP is the steepest descent path (SDP) or the gradient curve.[2–4]

Another pathway is the former distinguished reaction coordinate which has later been generalized as a distinguished coordinate path[5,6] and finally refined as Newton trajectory (NT).[5–12] For this type of RP holds that at every point of the curve the gradient of the PES points into the same direction, a direction of a prescribed search vector. It causes that NTs should be taken into account for mechanochemical problems. They are adapted to the given direction of the external force and result in the so-called force displayed stationary points (FDSP) curve. Note that usually SDP and NT are different curves, in contrast to the claim of the commented paper.

2 Steepest descent and Newton trajectories

The paper[1] treats the study of the influence of mechanical force on suface adsorbents. The ansatz of a mathematical description by a constant force and a linear influence of the coordinates by Eqs.(1) and (2) of ref.[1] is the usual formula which is accepted in the community of mechanochemistry. One could repeat that the effective PES is

$$V_{\mathbf{f}}(\underline{\mathbf{r}}) = V(\underline{\mathbf{r}}) - \underline{\mathbf{f}}^T \underline{\mathbf{r}} , \tag{1}$$

with $V(\underline{\mathbf{r}})$ is the PES of the problem, $\underline{\mathbf{f}}$ is the external force, and $\underline{\mathbf{r}}$ is the coordinate of a current structure. To put the gradient equal to zero results in

$$\nabla_{\mathbf{r}} V_{\mathbf{f}}(\underline{\mathbf{r}}) = \underline{\mathbf{0}} = \underline{\mathbf{g}} - \underline{\mathbf{f}} , \tag{2}$$

thus one searches a point where the gradient of the old PES, $\underline{\mathbf{g}}$, has to be equal to the mechanochemical force, $\underline{\mathbf{f}}$. It should be the force that induces the dissociation process of interest. It holds for all coordinates $\underline{\mathbf{r}}$, not only for minima (Min) and transition states (TS). Eqs.(1) and (2) form the definition of the Newton trajectory[5–12] which describes the curve of the force displaced stationary points (FDSP). There is given and then fixed the force direction $\underline{\mathbf{e}}=(e_1,\ldots,e_N)^T$ with $|\underline{\mathbf{e}}|=1$ and full force $\underline{\mathbf{f}}=F\underline{\mathbf{e}}$. The variable parameter F describes the amount of the force, or the length of the force vector. That means for $F=0$ for example, that the gradient is zero, thus the initial and final points of the FDSPs are the Min and TS of the potential V.

However, for any $F \neq 0$ we get a changed effective PES with Eq.(1) for which we find other Min and TS. So, if F changes in a certain interval, we have a family of effective PES where every of them has other Min and TS, but the consecutive points of this curve characterize the FDSPs curve.

Of course, the former steepest descent path (SDP) from original TS to original Min also

changes. The FDSPs curve is, in general, not the SDP of the original PES. The assumption of the commented paper[1] that the SDP is the FDSPs curve, is false, in nearly all thinkable cases. Generally, the original SDP and the solution of Eq.(2) for different values of the parameter F, are different curves. On each effective PES generated for a fixed $\underline{e}$ vector with different F values the isocontours are different, thus it is not possible to define a unique SDP under changing F. For a fixed $\underline{e}$ vector and a fixed F value only one could follow the defined SDP.

3 Steepest descent

The understanding of the steepest descent (SD) itself of ref.[1] is questionable. The argument that orthogonal to the SDP one finds a zero component of the gradient is correct, however, it is not restricted to the SDP from the TS, the intrinsic reaction coordinate.[2,3] It holds everywhere on the PES – it is the definition of the gradient. It is like that the gradient points along the steepest descent, and thus does not have a component orthogonal to the steepest descent.

The treatment of ref.[1] concerning the Hessian also holds for all points of the PES. Contrary to the understanding of the authors of ref.[1] there is a two-dimensional example in the literature[11,13] that an SDP from a TS can go downhill the PES crossing a ridge on its pathway, a nose, where the curvature is negatively orthogonal to the SDP. Here the SDP is definitively not a valley, and indeed not a deep valley.

4 Optimal force direction

The ansatz of Eqs. (1) and (2) are formally open for many directions $\underline{e}$, and every other direction causes a change of the effective TS in a different kind. On every such NT we find the bond breaking point (BBP) which is often the aim of the external force, to overcome the barrier at all.[14–19] Here, reactions are controlled by the thermal energy driving the system over the energy barrier and thus have a temperature dependence. The situation here seems to be one in which the barrier is sufficiently reduced to allow it to proceed at room temperature.

Note nevertheless that there is usually an optimal BBP with the corresponding optimal force direction, $\tilde{\underline{e}}$, which needs the lowest amount of force, $\tilde{F}$, in comparison to other external forces. These BBPs are well known in the literature, however, they do not emerge in ref.[1] To calculate the direction pointing to the optimal BBP is usually the aim of an application of a mechanochemical calculation.

5   The used example of a 2D PES

We are wondering if the inset of Fig.2 of ref.[1] and the toy example of Fig.4 of ref.[1] are two different cases: they are rotated by 45°. The SDP of Fig.4 goes along another direction than the SDP of the inset of Fig.2.

We guess that the authors of ref.[1] have done the experiments along the correct picture of the inset of Fig.2, with the correct use of the Cu(100) coordinates.[20] Here emerges the question, what is the direction of 45°. Probably not the SD of Fig.4 along the $x = y$-pathway.
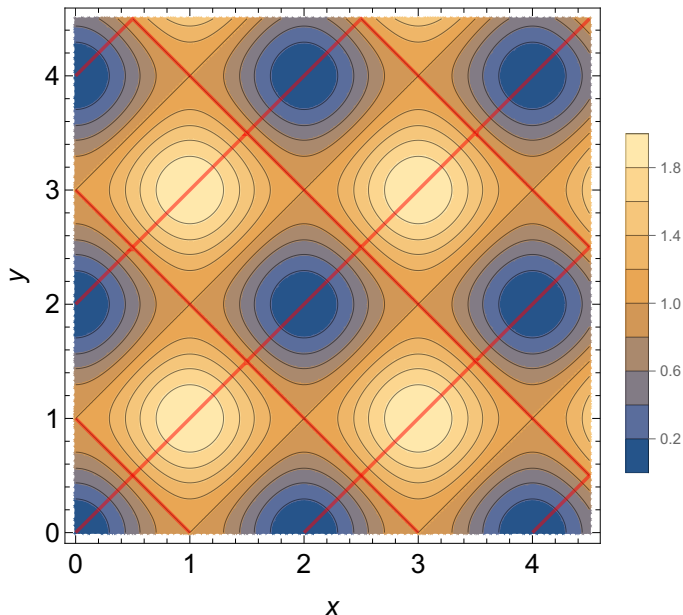

Figure 1: Singular NTs (red, along 45°) going into directions which connect minima and SPs of index 2 (maxima) on the R-P PES with parameter $r = 0$. The color bar depicts the levels of the PES.

Our Fig.1 shows the model R-P surface[1]

$$V(x,y) = 1 - cos(\pi(x+y)/2)cos(\pi(x-y)/2) \tag{3}$$

with parameters $r = 0$, $\alpha = 1$ and $E_{act} = 1$ of ref. [1] but with correct axes, x, y, for the Cu(100) foil. The red straight lines are NTs to the 45° direction. They depict a singular NT which bifurcates between the minima and the saddle points of index two into two side branches. The side branches lead on a constant level to the SPs of index 1. By the symmetry of the surface, the main branch of the NT from a minimum to a maximum is also a steepest descent line, however the bifurcation point hereon divides a valley and a hill along the pathway. We guess that the shear-induced pushing along the 45° direction goes along the main branch of the red NT.

One could speculate that the strange 45° direction observed in the experiment is caused from outside the 2D toy model of the R-P PES. We need more data from the other atoms, or molecular parts on the Cu surface which are already given in ref.[21] The breaking of a bond of the molecule, methyl thiolate, is connected with many distances and angles of the adsorbed molecule, many further internal degrees of freedom (DoF). Some of them may be of interest for the breaking of the sulfur bonds. Only a combined sight of Cu(100) and the other DoF may give a correct answer. However, other DoF are not discussed in ref.[1]

One could speculate that a kind of Morse curves is included in some of the additional DoF, the most simple potential curves. In Fig. 6 of ref.[21] one can observe that even the thermal molecular dynamics simulation of the carbon atom of the still adsorbed CH_3 species tends to move in one of the four 45° directions, off the sulfur center. If the shearing goes exactly into this direction then the dissociation may be enforced.

One could speculate that if the adsorbed remainder of the molecule slides along the minimum

energy path (MEP) of the Cu surface than we probably do not get a dissociation, however, only a sliding, from one Min to the next Min of the Cu surface.[22] This would not be the final aim of the treatment because one searches for a dissociation. If the real dissociation path goes over a maximum of the Cu surface to a greater extent, maybe then the dissociation can take place in a better way? Because, one does not need an MEP on the Cu surface, however, a dissociation path on the combined surface.

6   Conclusion

We agree with the first sentence of the introduction of ref.[1] that often the mechanochemistry is less well understood. We will give with this comment some thoughts for a better understanding. We observe an incorrect use of the R-P-PES[1] in comparison to the real Cu(100) surface. Then the authors of ref.[1] came to the conclusion that the SDP on the Cu(100) surface is the FDSPs curve of the interesting dissociation. The conclusion is, however, not correct. Both kinds of curves are usually different, here they are turned by 45°.

We propose a correct use of the R-P-PES and can propose that the measurements of ref.[1] of the real dissociation of the methyl groups may take place under a sliding over a maximum of the Cu(100) surface.

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Graphical TOC Entry

Optimal sliding direction of a pushing force depicts a singular Newton trajectory

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