

## RESEARCH ARTICLE

# Predicting Catalytic Efficiency of Nickel Nanoclusters: A Surface Activity Parameter Based Approach for Water Splitting

Moumita Dinda, Arijit Bag \*

**ABSTRACT:** Nickel nanoclusters are crucial catalysts in numerous organic and inorganic reactions. In this study, we theoretically investigate the water-splitting reaction on pristine nickel nanoclusters of varying sizes. We introduce a novel metric, the Surface Activity Parameter (SAP), to systematically assess the catalytic activity of nanoclusters. Our findings reveal that adsorption energy and activation energy for the water-splitting reaction exhibit a size-dependent trend. Specifically, as cluster size increases, adsorption energy becomes more negative, stabilizing the reactant molecules more effectively, while activation energy shows an increasing trend. The relationship between SAP and adsorption energy suggests an inverse correlation, indicating that smaller clusters exhibit higher catalytic efficiency. Furthermore, our analysis shows that the variation in SAP follows an exponential decay with increasing cluster size, demonstrating a predictable trend in catalytic behavior. The study also examines molecular interactions such as bond length elongation, vibrational frequency shifts, and Ni-O bonding characteristics post-adsorption, providing a mechanistic insight into the catalytic activity of nickel nanoclusters. The insights gained from this study could facilitate the rational design of efficient nanocatalysts for water-splitting applications.

**Keywords:** Nickel Nano Clusters; Surface Activity Parameter; Potential Energy Surface

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## 1. INTRODUCTION

Water splitting reaction is one of the most important reactions for green technology development. It is essential for steam reforming process [1], artificial photo-synthesis process [2], production of H<sub>2</sub> which is highly demandable as fuel for green energy generation [3], etc. The dissociative chemisorption of water on different catalyst surfaces is associated with the formation of H and OH which is an inevitable step for several catalytic processes like syngas synthesis, methane reforming, etc. Thus, an in-depth understanding of this process is being investigated by several researchers. Experimental studies regarding the water dissociation on transition metal catalyst surface are reported

in the recent years [4-6].

Hundt et al [7] reported a molecular beam study on D<sub>2</sub>O dissociation on Ni (111) surfaces. Their study indicates that the mode-selectivity is very important in this reaction. Their work was supported by quantum dynamical computation where the potential energy surface was constructed employing Density Functional Theory (DFT) study [8-10]. There are several groups involved in search of a better catalyst for water dissociation based on pristine transition metals and transition metal alloys [11-13]. Transition metals, particularly Ni and Ge catalysts, are used for water dissociation at present day laboratory research [14-16].

So far, water dissociation on different Ni surface (pure and doped) are reported [17-20]. Recently, a reaction dynamical study of water adsorption and dissociation on Cu/Ni bimetallic surface alloys are reported by Smita et al [21]. The catalytic efficiency of Ni-Cu bi-metallic surfaces depend on the ratio of these metals which is experimentally studied [22] There are also DFT study available in the literature regarding the catalytic efficiency of small Ni

Department of Applied Chemistry, Maulana Abul Kalam Azad University of Technology, West Bengal-741249, India.

\*Author to whom correspondence should be addressed:  
[bagarijit@gmail.com](mailto:bagarijit@gmail.com) (Arijit Bag)

clusters on Cu (111) surface for water gas shift reaction [23,24]. The presence of two different metals with large electrode potential difference, always tend to favor the dissociation of water thermodynamically. This is due to the stabilization of the H<sup>+</sup> and OH ions by the metal atoms. Thus, in addition to the Ni based alloys, various other combinations of noble metals (Pd, Pt, Ag, Ru, Ir), metal alloys with Ni as one component (Ni-Co, Ni-Mn, Ni-Mo), Ni sulfides and Ni phosphides are used as catalyst for water splitting process [25-31].

Among all surface catalysts tried so far, Pt and Pt-based systems show the highest activity still, the studies are going on to find out the best alternative to Pd and Pt based catalyst due to the high cost of Pd and Pt. To improve the catalytic efficiency of non-noble catalyst materials researchers, exploit different engineering strategies such as, the enhancing of catalyst surface area, varying the composition of the alloy catalysts, taking high catalyst loading, etc. In spite of several attempts, people are unable to find out an industrially usable catalyst. The key problem remains the same. Activities of the catalysts in this class decrease due to the formation of hydrides and the oxidative dissociation of the catalyst itself during the catalytic process [32].

To overcome these abridgments, researchers tried to decrease the Pt loading using Pt-shell nanomaterials within non-noble metal cores [33, 34] It will be interesting to look into how Ni-nanocluster incenses the dissociation of water. Therefore, we carried out a detailed DFT study to understand the effect of cluster size on the dissociation of water. There is no report available in the literature for the catalytic efficiency of Ni clusters of different size, for water splitting reaction. In the present research work we are prone to investigate the effect of cluster size of Ni cluster on the water splitting reaction. It is obvious that catalytic efficiency of a nano-cluster must vary from the surface. But how it will affect is a subject of concern. Also, there is no report regarding the dissociation of water on supported Ni clusters, though, alumina supported Ni clusters are used for different catalytic reactions [35,36].

In this research article, an attempt has been made to find out an appropriate parameter, Surface Activity Parameter (SAP), to predict the catalytic efficiency of any cluster from its cluster size. This would help to understand the role of surface activity of a cluster or solid surface in any catalytic process which is very essential for designing of catalyst as well as the choice of support.

## 2. COMPUTATIONAL DETAILS

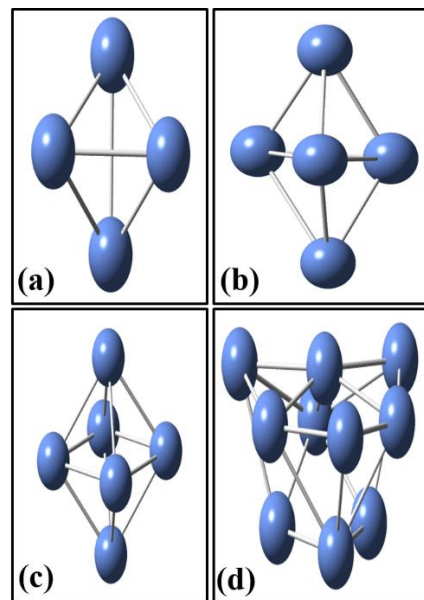
Optimization of Ni clusters, adsorption of water molecule on the nano clusters and all transition states are carried out using GAUSSIAN 09 [37] package. Potential energy surfaces for the water dissociation reaction path on different nanoclusters are constructed using this package. For these calculations B3PW91 [38-41] functional and cc-pVDZ [42] basis are used. For the comparison of catalytic activities of these catalysts,

the potential energy surface along the reaction path for different clusters are compared. Surface Activity Parameter (SAP) of different clusters are also computed and compared. Bond length, bond angles and O-H bond vibration frequencies are also computed to compare the activation of water molecule by different clusters.

## 3. RESULT AND DISCUSSION

### 3.1. Binding energies and Surface Activity Parameter (SAP) of nickel nanoclusters

Ni<sub>4</sub>, Ni<sub>5</sub>, Ni<sub>6</sub> and Ni<sub>10</sub> clusters are chosen for this study. The geometries of these clusters are taken from the literature [43,44]. All the clusters are optimized using GAUSSIAN 09 package at B3PW91/cc-pVDZ level of theory. The reaction free energies of formation of these clusters are presented in Table 1. It is observed that binding energy per atom increases with the increase of number of atoms except for Ni<sub>5</sub>. For Ni<sub>5</sub>, binding energy per atom is less compare to all other clusters. This may be due to the trigonal bi-pyramidal structure of this cluster (presented in Figure 1) where two atoms which are positioned at the opposite pyramidal top, are loosely bounded.



**Fig. 1.** Optimized geometries of Ni nanoclusters (a) Ni<sub>4</sub>, (b) Ni<sub>5</sub>, (c) Ni<sub>6</sub>, (d) Ni<sub>10</sub>.

It is obvious that, binding energy per atom is not the only deciding factor for the high activity of nano-clusters. Thus, a new parameter is introduced which is termed as Surface Activity Parameter (SAP), for the comparison of activity of different clusters. SAP is defined as follows:

$$SAP = \frac{(BE_{A_{bulk}} - BE_{A_{cluster}})}{\text{surface area}} \quad (1)$$

Where,  $BEA_{\text{bulk}}$  is the binding energy per atom in bulk and  $BEA_{\text{cluster}}$  is that of the cluster. Since, we are dealing with the pristine clusters only,  $BEA_{\text{bulk}}$  is same for all clusters. It is obvious that  $BEA_{\text{bulk}}$  will differ for different nickel crystals. But, they would differ marginally. Thus, if we take  $BEA_{\text{bulk}}$  for any crystal that would not affect the outcome of the calculation significantly.

SAP of these clusters were calculated to test whether this parameter is effective to predict the activity of a nano-cluster appropriately. Computed results are presented in Table 1. For this calculation  $BEA_{\text{bulk}}$  for Ni (111) crystal is used which is taken from the literature [21]. From the computed results it is found that the SAP values decrease with the increase of the number of atoms in the clusters which is expected. A plot of SAP vs number of atoms is presented in Figure 2. It shows that the decrease of SAP with respect to the number of atoms in a cluster, is an exponential decay type. A similar trend is observed for the surface area, presented in the same Figure. From these two observations it may be concluded that the surface activities of nickel clusters are very regular.

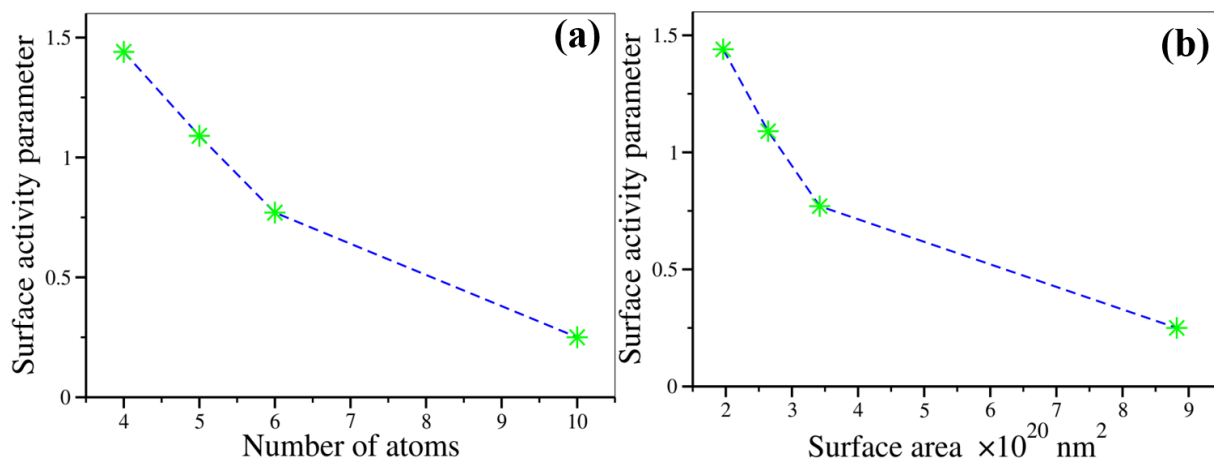
### 3.2. Comparative study of adsorption of water on different clusters

In case of heterogeneous catalyst, reactant molecules are

adsorbed on the catalyst surface. This influences the effect of catalyst on that particular reaction in two different ways. The adsorption energy contributes to the reaction energetics. A negative adsorption energy reduces the effective energy of activation i.e. the energy released by adsorption is supplied to the subsequent step of the reaction path. Due to adsorption, the reactant molecule gets activated by different mechanisms. A particular bond may be weakened, vibrational and rotational degrees of freedom is reduced due to adsorption which enhanced the reaction probabilities. Thus, the study of the change of properties of the reactants after the adsorption should be studied.

#### 3.2.1. Bond length and bond angle

The adsorption energy, change of O-H bond length, H-O-H bond angle and vibrational frequencies are studied for different clusters which are reported in Table 2. It is observed that due to adsorption on the nickel clusters, O-H bond length of water increased by 1pm by  $Ni_4$ ,  $Ni_5$  and  $Ni_6$  clusters and 2pm by  $Ni_{10}$  cluster with respect to the free water molecule. But, the increase of H-O-H bond angle is a function of cluster size. Bond angle increases gradually with the increase of cluster size. For  $Ni_{10}$  cluster, bond angle is the highest ( $112.1^\circ$ ).



**Fig. 2.** Variation of SAP with cluster size and surface area of the clusters.

**Table 1.** Free energies of cluster formation and other cluster parameters.

Number of atoms	Cluster diameter (nm)	Binding energy per atom (eV)	Surface area ( $\times 10^{20} \text{ nm}^2$ )	SAP* ( $\times 10^{20} \text{ eV nm}^{-2}$ )
4	0.25	2.409	1.96	1.44
5	0.29	2.350	2.64	1.09
6	0.33	2.586	3.42	0.77
10	0.53	3.02	8.83	0.25

\* $BEA_{\text{bulk}} = 5.23 \text{ eV}$  (for Ni(111) crystal<sup>21</sup>)

**Table 2.** Change of molecular properties of water due to adsorption.

H <sub>2</sub> O (cluster)	Adsorption energy (eV)	Ni–O bond lengths (Å)	O–H bond lengths (Å)	H–O–H angle	Vibrational frequencies of H <sub>2</sub> O (cm <sup>-1</sup> )		
					Bending	Stretching (Sym.)	Stretching (Anti-sym.)
H <sub>2</sub> O (free)			0.96, 0.96	102.6°	1660.2	3793.8	3898.2
H <sub>2</sub> O (Ni <sub>4</sub> )	-0.575	2.00	0.97, 0.97	103.8°	1615.5	3707.9	3796.9
H <sub>2</sub> O (Ni <sub>5</sub> )	-0.726	1.96	0.97, 0.97	104.0°	1606.4	3672.6	3765.3
H <sub>2</sub> O (Ni <sub>6</sub> )	-0.798	1.96	0.97, 0.97	104.5°	1605.0	3710.5	3804.4
H <sub>2</sub> O (Ni <sub>10</sub> )	-1.762	1.97	0.98, 0.98	112.1°	1594.9	3694.9	3838.5

### 3.2.2. Vibrational frequencies

The change of vibrational frequencies of water molecule due to the adsorption is very interesting. There is no straight forward variation. Different clusters influence different mode of vibration of water molecule in different extend. The change of the bending mode of vibration of the water molecule after adsorption on the nickel clusters follows a simple trend. The frequencies of the bending mode of vibration decrease with the increase of cluster size which is opposite to the trend of SAP value change which is presented in Table 1. It also contradicts with our common thinking that highly active cluster must affects more on the vibration of adsorbed water molecule. Thus, we try to find out a possible explanation of it.

It is observed that the Ni-O bond distance is highest for Ni<sub>4</sub> cluster and its effect on bending mode of vibration of water molecule is less among four clusters. The Ni-O bond distances are nearly same (differs at third decimal point: Ni<sub>5</sub> -1.963Å and Ni<sub>6</sub> - 1.965Å) for Ni<sub>5</sub> and Ni<sub>6</sub> clusters and bending mode of vibrational frequencies are also very close for these two clusters, 1606 and 1605 cm<sup>-1</sup> respectively. Thus, we may conclude that with the increase of cluster size, the shape of the cluster changes which allows to come the water molecule closer to the nickel atom which restrict the bending vibration of the water molecule.

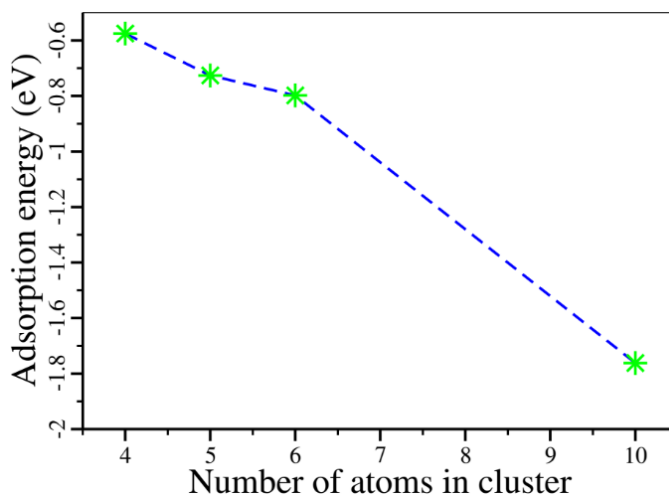
However, this conclusion is refuted by Ni<sub>10</sub>. Ni-O bond length in Ni<sub>10</sub> H<sub>2</sub>O adduct is 1.97Å but the bending mode of vibration of water molecule in this adduct is highly affected. The change of vibrational frequency is nearly 65 cm<sup>-1</sup>. Is it an anomaly or our conclusion made from the observations of other three clusters is wrong? We re-investigate these phenomena at the molecular level. It is found that while the plane of bending vibration of water molecule is nearly perpendicular to the Ni-O bond for Ni<sub>4</sub>, Ni<sub>5</sub> and Ni<sub>6</sub> clusters, that of the Ni<sub>10</sub> cluster is in a parallel position.

Thus, though Ni-O bond length is larger in Ni<sub>10</sub> cluster compare to Ni<sub>5</sub> and Ni<sub>6</sub> clusters, bending mode of vibrational frequency is decreased by a huge margin. The change of stretching frequency of water molecule due to adsorption on nickel cluster does not follow any trend. The symmetric stretching of vibration decreases significantly due to adsorption. The amount of decrease is nearly same for Ni<sub>4</sub>, Ni<sub>6</sub> and Ni<sub>10</sub> clusters which are 86, 83 and 99 cm<sup>-1</sup>. But, the

decrease of symmetric stretching frequency for Ni<sub>5</sub> cluster is more than 121 cm<sup>-1</sup>. A similar trend is observed for the anti-symmetric stretching mode of vibration. For this case, decrease of vibration frequency for Ni<sub>5</sub> cluster is maximum which is ~134 cm<sup>-1</sup>. However, for the anti-symmetric stretching mode of vibration, amount of decrease in frequencies of other clusters are different for different clusters which is not observed in the case of symmetric stretching mode of vibration. Here, the bigger cluster, Ni<sub>10</sub>, shows the lowest amount of decrease in vibrational frequency which is only 60 cm<sup>-1</sup>. The decrease of frequencies for Ni<sub>4</sub> and Ni<sub>6</sub> are 102 and 94 cm<sup>-1</sup> respectively.

### 3.2.3. Adsorption energy

There is another interesting observation regarding the adsorption energy of water on different clusters. Adsorption energy increases (absolute value) with the increase of cluster size which is exactly opposite to the order of SAP. This indicates that there is a definite orbital overlap between hydrogen atoms and their neighbor nickel atoms (except nickel atom which is bonded to oxygen atom) which decreases with the increase of cluster size. As a result, water molecule gets more stabilization due to adsorption. A plot of adsorption energy vs cluster size is presented in Figure 3.

**Fig. 3.** Variation of absorption energy with cluster size.

**Table 3.** Activation energies and dissociation energies of water on different clusters.

Cluster	Activation energy (eV) (from adsorbed state)	Effective activation energy (eV)	Water splitting energy (eV)
Ni <sub>4</sub>	0.316	-0.259	-1.025
Ni <sub>5</sub>	0.469	-0.257	-0.955
Ni <sub>6</sub>	0.976	-0.178	-0.854
Ni <sub>10</sub>	1.436	-0.326	-0.757

**Table 4.** Relation between SAP and adsorption energy.

Cluster (I)	Adsorption energy (eV) (II)	SAP (III)	II × III	I × II × III
Ni <sub>4</sub>	-0.575	1.44	0.828	3.312
Ni <sub>5</sub>	-0.726	1.09	0.791	3.955
Ni <sub>6</sub>	-0.798	0.77	0.615	3.69
Ni <sub>10</sub>	-1.762	0.25	0.431	4.31

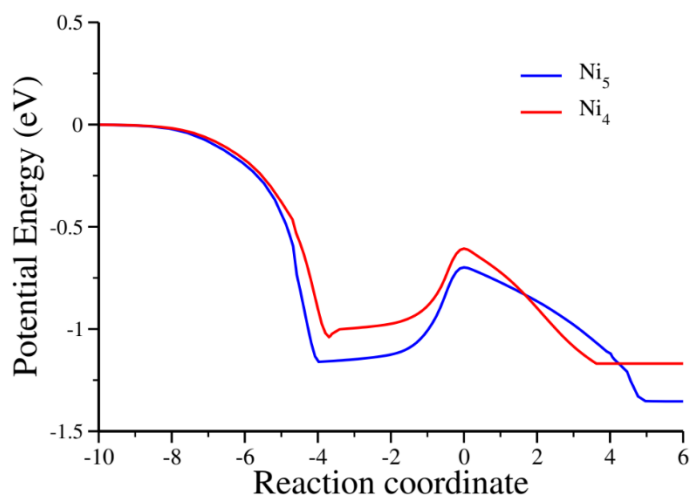
It is observed that the variation of adsorption energy with cluster size is not linear. The nonlinearity appears when number of atoms in the cluster is less. Thus, there may be any other effect which controls the stabilization energy. Ni-O bond distance may be one such parameter. For Ni<sub>4</sub>, Ni<sub>5</sub> and Ni<sub>6</sub>, variation of adsorption energy is similar to the variation of Ni-O bond. But adsorption energy is larger for Ni<sub>10</sub> than Ni<sub>5</sub> and Ni<sub>6</sub> though Ni-O bond distance of Ni<sub>10</sub> is larger compare to that of other two nickel cluster. This may be due to the neighboring nickel atom effect which is stated earlier.

### 3.3 Activation energy of water dissociation on different clusters

In section 3.2, we observed that water molecule is activated due to the adsorption on different Ni clusters. Thus, we study the catalytic activity of these clusters for water splitting reaction. We compute activation energy and reaction free energy for this reaction for each cluster presented in section 3.1. Computed results are shown in Table 3. It is observed that activation energy increases with the increase of cluster size which is expected and same as the SAP values presented in Table 1.

Previously, we observed that adsorption energy increases with the increase of cluster size, thus, we compute the effective activation energy for water splitting which is negative for most of the cases except Ni<sub>6</sub>. This is very interesting. This observation suggests that water would split immediately as soon as it gets adsorbed for most cases. Though, the overall splitting energy decreases with the increase of cluster size which is no surprise. Since, overall activation energy of water splitting energies are negative for Ni<sub>4</sub> and Ni<sub>5</sub> are negative, we study the potential energy surface along the reaction path for these two clusters which is shown in Figure 4. The nature of the surface for both

clusters are same. Since, adsorption energy of Ni<sub>5</sub> cluster is high (more negative value) it appears below the Ni<sub>4</sub> cluster (Table 4).

**Fig. 4.** Potential energy surface along the reaction path for water splitting on Ni<sub>4</sub> and Ni<sub>5</sub>.

## 4. CONCLUSION

This study provides a comprehensive analysis of the size-dependent catalytic properties of nickel nanoclusters for water splitting. A key outcome is the introduction of the Surface Activity Parameter (SAP), which successfully quantifies the catalytic efficiency of different nanocluster sizes. Our findings suggest that while smaller clusters exhibit higher SAP values, indicating greater catalytic potential,

adsorption energy trends inversely, stabilizing reactant molecules more effectively in larger clusters. However, the interplay between these two parameters is not linear. The product of SAP and adsorption energy varies across cluster sizes, suggesting that additional factors influence catalytic activity. Interestingly, when SAP, adsorption energy, and the number of atoms in a cluster are combined, they yield a near-constant value across different clusters, revealing an intrinsic relationship that governs nanocatalyst efficiency. Furthermore, the study highlights how molecular interactions, such as bond length elongation and vibrational frequency shifts, are influenced by cluster size, impacting the overall catalytic performance. The activation energy for water splitting increases with the decrease in SAP, aligning with the observed trends in adsorption energy. These insights not only enhance our understanding of cluster-size-dependent catalysis but also provide a framework for designing efficient nickel-based nanocatalysts. The SAP metric introduced in this work offers a promising approach for predicting and optimizing catalytic performance, paving the way for future experimental and theoretical explorations in nanoscale catalysis for sustainable energy applications.

## DECLARATIONS

### Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

### Funding

Not applicable

### Availability of data and material

All of the data obtained or analyzed during this study is included in the report that was submitted.

### Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

### Authors' contributions

Both authors contributed equally in the preparation of this manuscript.

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