

## Adsorption of Small Molecules on Metallic Surfaces

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### Abstract

The framework of adsorption of small molecules on metallic surfaces has been considered and the available experimental data have been analyzed.

### 1.Introduction

The activation of small molecules on well defined metallic surfaces has been the subject of many investigations [1]. The earlier work on this has been adequately summarized in Trapnell's book [2] on Chemisorption and the same has been reproduced in Table 1 for immediate reference. It is seen that the main objective of this table is to delineate the metals that will absorb the six typical molecules chosen and to rationalize the metals in terms of their

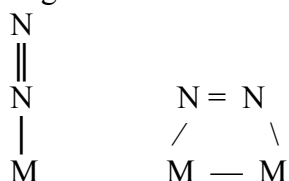
adsorption capabilities. The phenomenon of adsorption has always been associated with the concept of active centres originally proposed by Taylor. The adsorption of these simple molecules has been visualized in terms of some structural models and some of them are shown in Fig.1. However, these structural models are postulated based on bonding characteristics of these molecules in single molecular entities.

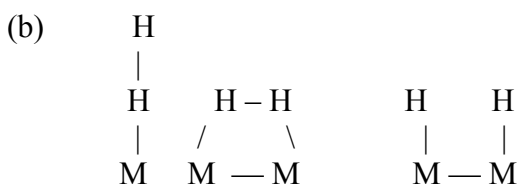
Table 1: The activities of the metal films in chemisorption (+ gets chemisorbed: - not chemisorbed [Reproduced from ref 2]

Group	Metals	Gases					
		N <sub>2</sub>	H <sub>2</sub>	CO	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	O <sub>2</sub>
A	W,Ta,Mo,Ti,Zr,Fe,Ca,Ba	+	+	+	+	+	+
B	Ni,Pt,Rh,Pd	X	+	+	+	+	+
C	Cu,Al	X	X	+	+	+	+
D	K	X	X	X	X	+	+
E	Zn,Cd,In,Sn,Pb,Ag	X	X	X	X	X	+
F	Au	X	X	+	+	+	X

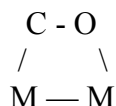
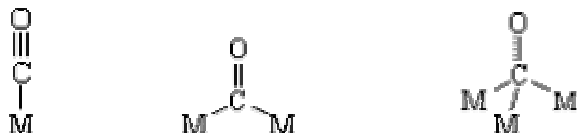
Fig.1. Some of the proposed structural models for the adsorption of simple molecules

(a) Nitrogen

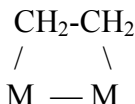




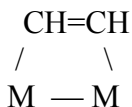
(C) Carbon monoxide



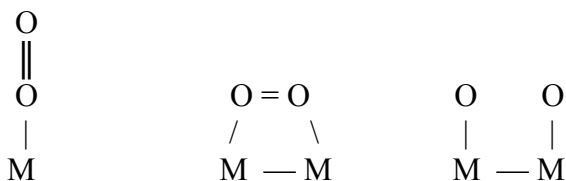
(d) Ethylene



(e) Acetylene



(f) Oxygen



The experimental data on the chemisorption of gases are mostly accounted for in terms of these models proposed. It is not possible to discuss all the experimental data reported in literature for the adsorption of all these gases, some of the essential trends are alone considered.

**(a) Chemisorption of Hydrogen (H<sub>2</sub>)**

In the H<sub>2</sub> molecule, the valence electrons are involved in the H-H σ-bond. The interaction with the surface has necessarily involved the same sigma bond electrons as there are no additional electrons specifically for this interaction. Consequently, chemisorption of hydrogen on metals is almost invariably

a dissociative process in which the H-H bond is broken, thereby permitting the hydrogen atoms to independently interact with the substrate. The adsorbed species in this instance therefore are hydrogen atoms.

The exact nature of the adsorbed hydrogen atom complex is generally difficult to determine experimentally, and the very small size of the hydrogen atom does mean that migration of hydrogen from the interface into sub-

surface layers of the substrate can occur with relative ease on some metals (e.g. Pd, rare earth metals).

The possibility of molecular H<sub>2</sub> chemisorption at low temperatures cannot be entirely excluded, however, as demonstrated by the discovery of molecular hydrogen transition metal compounds, such as W ( $\eta^2\text{-H}_2$ )(CO)<sub>3</sub>(Pi-Pr<sub>3</sub>)<sub>3</sub>, in which both atoms of the hydrogen molecule are coordinated to a single metal centre

Table 2. Typical data on the heat of chemisorption of hydrogen on metal surfaces computed by the CFSO BEBO model calculation are given in Table.1 together with other data reported in literature.

Metal	Crystal structure	Q exp	Q <sup>1</sup> (cal)	Q <sup>2</sup> (cal)	Q <sup>Eley</sup>	Q <sup>Stvn</sup>	Q <sup>trst</sup>
Ti	Cph	38.9	45	38[40]			48.2
V	Bcc		48	45			
Cr	Bcc	45	41	38[36]	16	24	38.4
Mn	Bcc		43	36			
Fe	Bcc	32.8*	30	32[32]	17	31.6	34.4
Co	Fcc	24±4	23	24[28]		31.0	
Ni	Fcc	27.5*	23	24[27]		28.9	33.6
Zr	Cph		60	50			
Nb	Bcc		60	58			
Mo	Bcc	40	44	46[45]		42.9	50.9
Tc	Cph		28	31			
Ru	Cph	26±2	24	28[30]		38.1	
Rh	Fcc	25.6*	22	25[26]	24	32.3	
Pd	Fcc	26	15	18[22]		22.5	27.2
Hf	Cph		74	59			
Ta	Bcc	45	71	67[50]	32	49.6	56.8
W	Bcc	48.7*	60	61[45]	44	45.6	53.2
Re	Cph		32	36			
Os	Cph		30	34			
Ir	Fcc	26±2	26	30[24]		38.1	
Pt	Fcc	24*	22	25[25]		22.6	29.1

\* these values are average values of the available experimental data; [ data] are from ref 7; Q<sup>Eley</sup>, Q<sup>Stvn</sup>, Q<sup>trst</sup> denote the values obtained by Eley[4], Stevensen[5] and Trasatti [6] respectively. The Q<sup>1</sup> and Q<sup>2</sup> are the values calculated from the two equations respectively

$$E_{\text{Ms-A}_s}^1 = (\beta E_{\text{M-M}} + E_{\text{A-A,s}})/2 + 23 [\gamma \chi_{\text{M}} - \chi_{\text{A}}]^2$$

$$E_{\text{Ms-A}_s}^{11} = (\delta(E_{\text{M-M}} + E_{\text{A-A,s}})/2 + 23 [(\chi_{\text{M}} - \chi_{\text{A}})^2])$$

### (b) Chemisorption of Nitrogen and Oxygen (O<sub>2</sub> and N<sub>2</sub>)

Oxygen is an example of a molecule which usually adsorbs dissociatively, but is also found to adsorb molecularly on some metals (e.g. Ag, Pt). In those cases where both types of adsorption are observed it is the dissociative process that corresponds to the higher adsorption enthalpy.

In the molecular adsorption state, the interaction is relatively weak. Molecules aligned such that the internuclear axis is parallel to the surface plane may bond to a single metal atom of the surface via both

1.  $\sigma$ -donor interaction, in which the charge transfer is from the occupied molecular  $\pi$ -bonding molecular orbital of the molecule into vacant orbitals of  $\sigma$ -symmetry on the metal (i.e.  $M \leftarrow O_2$ ), (conventionally known as donation) and
2.  $\pi$ -acceptor interaction, in which an occupied metal  $d$ -orbital of the correct symmetry overlaps with empty  $\pi^*$  orbitals of the molecule and the charge transfer is from the surface to the molecule (i.e.  $M \rightarrow O_2$ ). (conventionally known as back donation)

Although the interaction of the molecule with the surface is generally weak, one might expect that there might be a substantial barrier to dissociation due to the high strength (and high dissociation enthalpy) of the O=O bond. Nevertheless on most metal surfaces, dissociation of oxygen is observed to be facile which is related to the manner in

which the interaction with the surface can mitigate the high intrinsic bond energy and thereby facilitate dissociation.

Oxygen atoms are strongly bound to the surface and will tend to occupy the highest available co-ordination site. The strength of the interaction between adsorbate and substrate is such that the adjacent metal atoms are often seen to undergo significant displacements from the equilibrium positions that they occupy on the clean metal surface. This displacement may simply lead to a distortion of the substrate surface in the immediate vicinity of the adsorbed atom (so that, for example, the adjacent metal atoms are drawn in towards the oxygen and the metal-oxygen bond distance is reduced) or to a more extended surface reconstruction.

Dissociative oxygen adsorption is frequently irreversible - rather than simply leading to desorption, heating of an adsorbed oxygen overlayer often results in either the gradual removal of oxygen from the surface by diffusion into the bulk of the substrate (e.g. Si(111) or Cu(111)) or to the formation of a surface oxide compound. Even at ambient temperatures, extended oxygen exposure often leads to the nucleation of a surface oxide. Depending on the reactivity of the metal, further exposure at low temperatures may result either in a progressive conversion of the bulk material to oxide or the oxidation process may effectively stop after the formation of a passivating surface oxide film of a specific thickness (e.g. Al).

### Nitrogen

The interaction of nitrogen with metal surfaces shows many of the same

characteristics as those described for oxygen. However, in general  $N_2$  is less susceptible to dissociation as a result of the lower M-N bond strength and the substantial kinetic barrier associated with breaking the  $N\equiv N$  triple bond.

### (C) Chemisorption of Carbon Monoxide

Depending upon the metal surface, carbon monoxide may adsorb either in a molecular form or in a dissociative fashion - in some cases both states coexist on particular surface planes and over specific ranges of temperature.

1. On the reactive surfaces of metals from the left-hand side of the periodic table (e.g. Na, Ca, Ti, rare earth metals) the adsorption is almost invariably dissociative, leading to the formation of adsorbed carbon and oxygen atoms (and thereafter to the

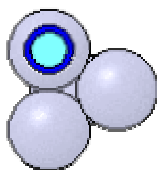
formation of surface oxide and oxy-carbide compounds).

2. By contrast, on surfaces of the metals from the right hand side of the  $d$ -block (e.g. Cu, Ag) the interaction is predominantly molecular; the strength of interaction between the CO molecule and the metal is weaker, so the M-CO bond may be readily broken and the CO desorbed from the surface by raising the surface temperature without inducing any dissociation of the molecule.
3. For the majority of the transition metals, however, the nature of the adsorption (dissociative versus molecular) is very sensitive to the surface temperature and surface structure (e.g. the Miller index plane, and the presence of any lower coordination sites such as step sites and defects).

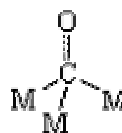
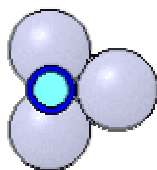
Molecularly chemisorbed CO binds in various ways to single crystal metal surfaces - analogous to its behaviour in isolated metal carbonyl complexes.



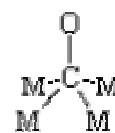
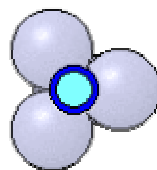
Terminal ("Linear")  
(all surfaces)



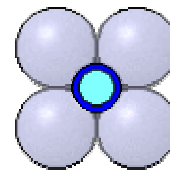
Bridging (2f site)  
(all surfaces)



Bridging / 3f hollow  
(*fcc*(111))



Bridging / 4f hollow  
(rare - *fcc*(100)?)



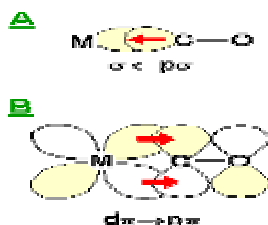
Whilst the above structural diagrams amply demonstrate the inadequacies of a

simple valence bond description of the bonding of molecules to surface, they do

to an extent also illustrate one of its features and strengths - namely that a given element, in this case carbon, tends to have a specific valence. Consequently, as the number of metal atoms to which the carbon is co-ordinated increases, so there is a corresponding reduction in the C-O bond order.

However, it must be emphasized that a molecule such as CO does not necessarily prefer to bind at the highest

available co-ordination site. So, for example, the fact that there are 3-fold hollow sites on an *fcc*(111) surface does not mean that CO will necessarily adopt this site - the preferred site may still be a terminal or 2-fold bridging site, and the site or site(s) which is(are) occupied may change with either surface coverage or temperature. The energy difference between the various adsorption sites available for molecular CO chemisorption appears to be very small.



The reduction in the stretching frequency of terminally-bound CO from the value observed for the gas phase molecule (  $2143 \text{ cm}^{-1}$  ) can be explained in terms of the Dewar-Chatt or *Blyholder model* for the bonding of CO to metals.

This simple model considers the metal-CO bonding to consist of two main components:

**A** : this is a  $\sigma$  bonding interaction due to overlap of a filled  $\sigma$  -"lone pair" orbital on the carbon atom with empty metal orbitals of the correct symmetry - this leads to electron density transfer from the CO molecule to the metal centre.

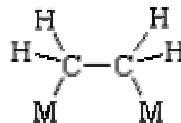
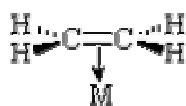
**B**: this is a  $\pi$  bonding interaction due to overlap of filled metal  $d\pi$  (and  $p\pi$  ) orbitals with the  $\pi^*$  antibonding molecular orbital of the CO molecule.

Since this interaction leads to the introduction of electron density into the CO antibonding orbital there is a consequent reduction in the CO bond strength and its intrinsic vibrational frequency (relative to the isolated molecule).

### (D) Chemisorption of Unsaturated Hydrocarbons

Unsaturated hydrocarbons (alkenes, alkynes) all tend to interact fairly strongly with metal atom surfaces. At low temperatures (and on less reactive metal surfaces) the adsorption may be molecular, albeit perhaps with some distortion of bond angles around the carbon atom.

Ethene, for example, may bond to give both a  $\pi$ -complex (**A**) or a di- $\sigma$  adsorption complex (**B**):



(A) *Chemisorbed* (B)  
*Ethene*

As the temperature is raised, or even at low temperatures on more reactive surfaces (in particular those that bind hydrogen strongly), a stepwise dehydrogenation may occur. One particularly stable surface intermediate found in the dehydrogenation of ethene is the *ethylidyne* complex, whose formation also involves H-atom transfer between the carbon atoms.

Based on the data available at this stage, the metals can be classified into four groups on the basis of adsorption of these molecules either in molecular and/or dissociative form. One such classification is given in Table 3.

Table. 3 :Classification of transition d-metals based on adsorption properties [3]

Group	Metals	Adsorption state									
		Dissociative form					Nondissociative form				
		H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	NO	CO	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	NO	CO
A	Hf, Ta, Zr Nb, W, Ti, V Mn, Cr, Mo	P	P	P	P	P	I	I	I	I	I
B	Fe, Re	P	P	P	P	P	I	I	I	P	P
C	Ni, Co, Tc	P	P	I	P	P	I	I	I	P	P
D	Os, Ir, Ru Pt, Rh, Pd	P	P	I	P	I	I	I	I	P	P

P- Possible I- Impossible

There are a variety of spectroscopic techniques that have been employed to study the chemisorption of gases on metallic surfaces. We shall consider only the adsorption of CO and outline the type of results obtained.

1. **Thermal Desorption Spectroscopy (TDS)**[8]: For example the typical TDS spectrum for CO adsorption on typical metals has shown up to five desorption peaks designated as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$  and usually the earlier peaks are attributed to desorption

from multilayers and the last three are associated with desorption from monolayer. This deduction is made on the basis of the amount of CO desorbed and also from the desorption energies usually deduced from TD spectra obtained at various heating rates or from other variables. Usually the  $\epsilon$  state desorbs over a wide temperature range and hence has to be associated with a single chemisorbed state but the chemisorption energy though may be assigned one single value, really means that desorption takes place with a spectrum of energies and hence the adsorbed species cannot be assigned to one single adsorbed molecular species. The spectrum of desorption energies can arise either due to the variations in the adsorption bond or due to repulsive interactions among the adsorbed species. Therefore one has to be realize that the FWHM reflects on the desorption energies involved and hence there is no unique adsorbed species and one has a gradual variation of adsorption energies for the adsorbed species.

2. **Photoelectron spectroscopic measurements:** The Ultraviolet photoelectron spectra are usually resorted to for identifying the non-dissociative adsorption of gases, since the changes in the binding energy of the molecular orbitals of the adsorbate can be a measure of the strength of the bonding of the adsorbate to the surface. Some typical data reported in literature are summarized in Table In the case of non dissociative adsorption of carbon monoxide on metals; one would

examine the position of the photoemission peaks of  $5\sigma$ ,  $1\pi$  and  $4\sigma$  levels of carbon monoxide since they are the frontier orbitals. Conventionally according to the **Blyholder model** which has been outlined earlier, in the adsorbed state the separation between  $1\pi$  and  $5\sigma$  levels are considerably reduced and even the relative positions are interchanged and the position of the  $4\sigma$  level is altered considerably. The observation of these molecular energy levels in the photo-emission spectra is considered as a fingerprint for identifying the non dissociative (molecular) nature of adsorption and the extent of the shift is considered as a reflection of the strength of bonding. Though these interpretations are well accepted and also appear to account for many of the observations, it should be pointed out that the eigen functions of the orbitals are certainly lost their molecular identity when interacting with the surface and hence the binding energy positions of the orbitals could have been considerably altered on interaction with the wave functions of the surface. In this case, one is not sure how much of the binding energy change is due to this orbital mixing and how much is due to the interaction energy. At best one can only assume that the trends of binding energy changes may be used to evaluate the relative order of interaction of the molecule with the surface. The absolute value of the change in binding energy may not be a suitable parameter to relate to the strength of the adsorption bond.

Table.4. UPS peak positions for CO/M for CO adsorption on typical metals { from ref 8}



Substrate	T[K]	hv[eV]	$\Theta$ [ML]	Peak positions [eV] and assignment				Bonding state		
Cu(poly)	20	40	$\sim 0.5$	8.7(5 $\sigma$ )		11.6 (1 $\pi$ )	14.5 (4 $\sigma$ )	Phy		
	30	40.8	.3	8.5(5 $\sigma$ /1 $\pi$ )		11.8 (4 $\sigma$ )	13.5s	Chem.		
Cu(100)	>77	90	(2x2)	8.6(5 $\sigma$ /1 $\pi$ )		11.5 (4 $\sigma$ )	13.5s	Chem.		
Ag(110)	50	40.8	<1	9.1(5 $\sigma$ )		11.9 (1 $\pi$ )	14.8 (4 $\sigma$ )	Phy		
	50	12.5	+1	9.5(5 $\sigma$ /1 $\pi$ )		12.1 (4 $\sigma$ )	14.8s	Chem.		
Au(poly)	77	40.8	0.2	9.8		12.3	13.3			
Au(110)	117	132.2	0.3	10.0(1 $\pi$ )		12.5 (4 $\sigma$ )	13.8s	Chem.		
	>77	150	<0.5	9.8(5 $\sigma$ /1 $\pi$ )		12.6 (4 $\sigma$ )	13.5s	Chem.		
	28	24	0.25	7.3 w	9.4	-	12.5 w	13.8-14.5 w	Chem.	
			0.5	7.7 w	9.4	10.3	12.5 w	13.8-14.5 w	13.3 (4 $\sigma$ )	Chem.
			1.0	7.8(5 $\sigma$ )	{9.3}	10.4 (1 $\pi$ )	12.5w	13.8-14.5 w	13.3 (4 $\sigma$ )	Phy
>2.0			8.2 (5 $\sigma$ )		11.2 (1 $\pi$ )			14.0 (5 $\sigma$ )	Cond	
Gas phase I.P.*			14.01(5 $\sigma$ )		16.91 (1 $\pi$ )		19.72 (5 $\sigma$ )			
I.P.- ( $\phi_0 + \Delta \phi$ )			9.59(5 $\sigma$ )		12.49 (1 $\pi$ )		15.30 (5 $\sigma$ )			

### 3) Over Layer Structures by Leed

A number of LEED patterns have been reported for almost all gases adsorbed on metallic surfaces. For CO adsorption a variety of LEED patterns are reported and also changes of LEED patterns as a function of coverage is well known. These patterns with various geometries especially the tilted geometries like ( $\sqrt{2} \times \sqrt{2}$ )R 30 are indications that localized bonding normally visualized in the form of adsorbed states shown in Fig 1 might not represent the true bonding and the wave function of the adsorbate overlaps with the various frontier wave functions of the surface and thus give rise to a series of adsorbed state LEED patterns. As the frontier orbital wave functions of the adsorbent can have different density centers it is possible that the adsorbed state geometries can vary with respect to coverage. It may be possible the whole set of LEED patterns observed with the adsorbed states can be arising out of the orbital overlaps of the surface with the valence orbitals of the adsorbate of

suitable energy and geometry and hence the model of localized bonding may be one of the extreme cases.

### 4) Work Function Measurements

Work function changes have been often interpreted in terms of electron exchange between the adsorbate and adsorbent and hence it is possible  $\Delta\phi$  can have both signs of variation. In the case of adsorption of CO in initial stages ( that is the  $\epsilon$  state) the work function of the adsorbate decreases indicating the population of the lowest unoccupied states of the adsorbent from the valence electrons of the adsorbate. The magnitude of the work function change will depend on the energy, symmetry and degeneracy of such states of the adsorbent. The relative gradient of the variation of the work function as a function of coverage is a reflection of the extent of the overlap of the orbitals of the adsorbent with that of the adsorbate and hence in this sense, this variation can be considered to be a

measure of the strength of the adsorption bond.

### 5) NEXAFS Measurements

The near edge spectrum reflects the emission from the occupied states of the adsorbate and it is usually considered that the first resonance observed for CO adsorption on metallic surfaces is assigned to  $\pi^*$  resonance and the next one to  $\sigma^*$  state of the CO. Even though these assignments reflect the overall symmetry of the wave functions from which the emission has been observed, and the shape of the resonance emission is a reflection of the alteration of the wave function due to overlap with the wave functions of the adsorbent. The variation of the shape of this resonance with coverage of the adsorbate is indication that the different energy and symmetry wave functions of the adsorbent overlap with the same wave function of the adsorbate.

### 6) Kinetics of Adsorption

The kinetics of adsorption on metallic surfaces has been treated in terms of various models. One of the models that have been extensively adopted is called the Elovich equation which has been used extensively to treat adsorption kinetic data. The mathematical form of Elovich equation is  $dq/dt = a \exp\{-bq\}$ . On integration the Elovich equation with boundary condition  $q=q$  at  $t=t$  and  $q=0$  at  $t=0$  becomes  $q = 1/b \ln\{1+abt\}$  and the linear form of Elovich equation is  $q=(1/b) \ln(ab) + (1/b) \ln\{t+t_0\}$  where  $a$  and  $b$  are parameters of the equation and  $t_0 = 1/ab$ . This equation was commonly used in the kinetics of chemisorption of gases on solids [9]. The Elovich equation has rarely been applied to liquid state sorption. Recently it has

been successfully used to describe the sorption of zinc ions on soils and also for the sorption of metal ions on solvent impregnated resins and other adsorptions and release of metal ions from soils.[10-13].It has even been used to analyze Thermal analysis[14] and also other phenomena [15]

The values of the two constants of this equation obtained from the slope and intercept of a plot of  $q$  versus  $\ln t$  have been interpreted in terms reflecting initial rate of the process and also the nature of sites involved in the adsorption process. The general explanation for this form of kinetic law involves a variation of the energetics of chemisorption with the extent of coverage [16]. Another plausible explanation could be that the active sites are heterogeneous in nature and therefore exhibit different activation energies for chemisorption. [16]. These two explanations have been extensively utilized to interpret the variations of the two constants of Elovich equation with experimental parameters like temperature and pressure. In the analysis of kinetic data of adsorption of gases on metals one has to take into account that most of the adsorption takes place in the initial period and only the final 10% of adsorption process follows the Elovich kinetic law. Even then this final adsorption kinetic data when analyzed by means of Elovich equation as a plot of  $q$  versus  $\ln t$  gives rise to gradient changes.

Even though the surface heterogeneity or variation of the energetics of adsorption with coverage are parameters of importance, their effect would have been more meaning for the initial fast adsorption than for the slow last 10% of adsorption which is analyzed through the Elovich equation. The species arising from the initial fast chemisorption could

have utilized most of the frontier orbitals of the adsorbent for overlap with the wave functions of the adsorbate and hence the charge density contours of the wave functions of the adsorbent involved in bonding with the last (slow) 10% adsorption could be associated with eigen values well below the frontier orbitals. Hence this process of interaction will require distinct changes as result of coverage which could have given rise to gradient changes and also not a uniform variation of the constants of the Elovich equation with experimental parameters since it is an inherent parameter of the system and not of the experimental variables.

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