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# A study on energy and time description of the catalytic act with the selective energy transfer and impulse oscillation models

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## Abstract

We suggest a physical picture of the catalytic act combining together the energy transfer and the synchronisation of the best electron density in the reactant and active site as a consecutive sequence of events. Activity and selectivity at molecular level are defined. Geometry requirements seem to be linked to energy and time requirements. Our proposal for developing new catalysts at the molecular level is to find the set of most profitable ranges of frequencies of the vibrators in an ideal catalytic system, predicted by combination of the SET and IOM models. In order to transform these results to a practical catalyst one can use quantum chemistry computation to characterise vibration modes of real systems for a wide range of variations. The shifts of the frequencies resulted from comparison of the calculated with the SET and IOM models frequencies and ones for non-interacting reactant and catalytic centre can serve as the base data in choice of the real systems. If, for one such system, the quantum chemistry calculated frequencies agree with the ones predicted from SET and IOM, a good catalyst is found. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Selective energy transfer; Impulse oscillation; Wavenumber

## 1. Introduction

Despite of rapid modern development of theory of catalysis, the practical use of the theory for computer-aided design of industrial new catalysts seems to be still a long-term goal [1]. Real catalytic reaction systems are too complicated for quantum chemistry ab initio methods. Therefore, a relatively simple conversion of molecular level description into real scale of catalytic reaction system is needed [1].

Most models of catalysis starts from the macroscopic observations and discuss the kinetic observa-

tions in terms of an assumption of the existence of active sites, with properties statistically distributed over the entire population of sites. Such models discuss acidity of sites, adsorption properties of sites, geometric distance between sites, sites with multiple bonding, etc.

If one wants to construct a really new catalyst, the reverse viewpoint must be considered. From some simple first principles one must deduce properties of the active site and how they affect the reactivity of the reactant(s).

One such method is the use of quantum chemistry. As said above, this approach is difficult in practice. Another method is to use some physical observables as the starting items and from this, more or less classical physics approach, deduce properties that can be related to experimental data in catalysis.

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Such observables are, e.g. the wavenumbers of the vibration modes of the reacting species, of the catalyst centre and of the products supposed to be formed. As the essence of a chemical reaction is the movement and reconfiguration of atoms in molecules we suggest to chose vibration modes of the molecular systems as the starting point.

## 2. The models of SET and IOM

In this paper we present a tool for computer-aided design of catalysts, based on two complementary models with vibrational modes as the primary molecular parameters for description of catalysis at molecular level. The first is the selective energy transfer (SET) model [2] which is able to distinguish that one of the vibrational modes of reactant molecule used as a “channel” for energy quanta flow from the heat bath to the molecule during its activation on a considered reaction path. The SET model is based on the idea of resonance between catalyst vibrators and the above-mentioned important mode of the reactant [2].

The second one is the impulse oscillation model (IOM) [3] which aims to calculate which of the vibrational modes in the reactant molecule and in the catalytic centre that are important for the considered catalytic act to occur. The basis of the model is the synchronisation of the best electron density distribution in the reactant and in the centre. From IOM computation the most important vibrational modes and the most profitable ranges of frequencies for the reaction to occur are obtained [4]. The IOM uses frequencies of a set of vibrators of a catalytic system to obtain the time of the synchronisation.

The following three aspects: energy, time and geometry of a catalytic system has been suggested as essential to describe catalysis [3]. While the geometry and energy aspects of catalytic systems are in the centre of interest of quantum chemistry modelling, the energy and time description of such systems is still to be developed. Notice, that in our models the same physical observables-frequencies are used as the measure of energy (SET) or the measure of time (IOM).

In previous works on HCOOH decomposition on oxide catalysts [5–7] that will be used as examples in the present paper we found that the same vibrators, most important for the reaction, are predicted by SET

and IOM models for the dehydrogenation reaction (the OCO bending mode) and for the dehydration reaction (the OCO asymmetric stretching mode). Thus, in these reactions the same vibrators simultaneously fulfil the conditions for energy transfer and for time of synchronisation.

The aim of our present study is to find a basis for the SET and IOM models generalisation. We will suggest a common physical picture of the catalytic act combining together the energy transfer and the synchronisation as a consecutive sequence of events.

## 3. Description of SET

The main assumption is that the reaction rate is determined by the effectiveness with which energy can be transferred to the reacting molecule from the surrounding heat bath.

This transfer is taking place by resonance between vibrators of the heat bath ( the catalyst )  $\omega$  and that specific vibrational mode  $\nu$  of the reacting molecule that most closely deforms the molecule towards the structure in the activated state.

Treating this resonance system as a classical forced, damped harmonic oscillator, and later on introducing the anharmonicity, one can arrive [2] at an expression for the rate constant (Eq. (1)) and from this a description of so called isokinetic temperature (Eq. (1a)),  $T_{\text{iso}}$ , should there exist an isokinetic effect in a series of closely related systems.

$$\ln k = \ln Z + \omega (\nu^2 - \omega^2)^{-1} \times \left[ \frac{\pi}{2} - \arctg \left( \frac{\nu\omega}{(\nu^2 - \omega^2)} \right) \right] \frac{E}{Nhc} - \frac{E}{RT} \quad (1)$$

$$T_{\text{iso}} = Nhc R^{-1} (\nu^2 - \omega^2) \omega^{-1} \times \left[ \pm \frac{\pi}{2} - \arctg(0.5\nu\omega(\nu^2 - \omega^2)^{-1}) \right]^{-1} \quad (1a)$$

The relation (1) refers to the empirical Arrhenius equation but for the second term on the right hand side, which refers to the selective energy transfer effect.  $T_{\text{iso}}$  is the temperature where the Arrhenius lines for a series of closely related systems intersect. Such a common point of intersection results in a linear relation between  $\ln A$  and  $E_a$ . ( $A$  and  $E_a$  are the pre-exponential

factor and the activation energy of the Arrhenius law, respectively).

The critical questions now appear: why has the activation energy,  $E_a$ , different values at all? And are  $E$  and  $E_a$  the same quantities? If structural conditions of the catalysts are such that the reacting bond has to be stretched (bent) to a certain extent on one catalyst and to a much larger extent on another catalyst, the activation energy will be larger in the latter case. As a consequence of this it follows that the activation energy for a series of closely related systems (e.g. the same reactant and slightly differing catalysts) will constitute a series of values, with an almost constant increment, the quantum of vibrational energy. A tentative answer to the second question is given in paper [8].

#### 4. Description of IOM

The impulse oscillation model (IOM) was developed [3] as a part of description (time requirements) of the complexity of catalytic molecular devices in a general model [9,10] named elementary catalytic system (ECS), where geometry, energy and time requirements have been considered. In the IOM it is assumed that a reaction runs when the favourable distribution of the electron density in the reacting molecule and in the catalytic centre appear at the same time. Such distribution is named the reactivity impulse. The periodical appearance (named oscillation) of the reactivity impulse is closely connected with the electron density redistribution during the vibrations of reacting molecules and the catalytic centre. These time parameters (vibrational periods) contain also information on energy, chemical composition and geometry of the oscillators.

The model is based on a set of Eq. (2) connecting the wavenumbers of the considered modes with discrete moments of simultaneous appearance (named synchronisation time) of such favourable distributions of electron density in the reactant and in the catalytic centre that the reaction can occur.

$$\frac{(w_1 + k_1 n_1)}{\nu_1} = \dots = \frac{(w_i + k_i n_i)}{\nu_i} \quad (2)$$

where  $\nu$  is IR frequencies,  $n$  integer number of vibration cycles,  $k$ ,  $w$  phase coefficients due to model formalism [4]. The number ( $i$ ) of equations is equal

to the number of chosen vibrational modes. Choice of the important modes results from an analysis of assumed mechanism of the reaction.

The parameterised Eq. (2) are computed on PC Pentium using our program IOMOS [11]. As the results possible wavenumber ranges for each of the modes, within which the synchronisation can be reached. In calculation wide ranges are use expanded to lower and higher wavenumbers in comparison to appropriate experimental ranges of previously known catalysts. In this way one cannot only test the results of calculation for the known catalysts but also find ways to improve the catalyst.

The resulting set of wavenumber ranges for the selected vibrational modes is used as input data in program IOMAB [12] to determine a selectivity of choice of one from two possible (A and B) paths. The program IOMAB finds subsets of the ranges where the synchronisation for only one way is possible (A or B) and the subsets where synchronisation for both paths is possible. In the later case IOMAB distinguishes a case when synchronisation time for the A path is shorter than for the path B (AB case) and a case when the time for path B is the shorter one (BA case). The selectivity of choice of the path A is calculated in the program IOMAB from the following formula:

$$Sa = \frac{(A + AB + BA) \times 100}{A + B + 2(AB + BA)} \quad (3)$$

where A, B, AB, BA are sums of the width (in wavenumbers) of ranges where the above described cases of synchronisation are possible.

Detailed description of methodology, set of programs for PC and examples of practical use of the IOM model was recently published [4].

#### 5. A physical model of catalysis at molecular level combined energy transfer and synchronisation

Let us consider the simplest catalytic reaction system containing a molecule of substrate (designated as  $S$ ) before a reaction, a catalytic centre ( $C$ ) and a molecule of product ( $P$ ) after a reaction. We ask what types of events in this system are necessary for the catalytic reaction to occur. It is useful to distinguish two types of elementary events. The first type (physical events) are connected with activation of the

molecule  $S$ , i.e. with energy flow from a reservoir of energy to the reactant  $S$ . The second one should result in chemical transformation of substrate  $S$  into product  $P$ .

What rules will govern the energy flow at molecular level? For the best catalyst the most effective energy transfer should occur. Therefore, we assume that all of the energy transferred to the substrate  $S$  should be easily fed into the part of the internal energy (of molecule  $S$ ) that is directly used for reaction. It means that for a vibrationally activated reaction the activation energy should be closely related to a sum of vibrational quanta of the substrate  $S$ . This is one of the main theses in the SET model. On the other hand, it is well-known that values of activation energy in a considered catalytic reaction strongly depend on catalysts used in the reacting system, i.e. each value is a particular attribute of appropriate catalytic centre. Therefore, one can say that the value of activation energy contains information on molecular energy properties of both the substrate  $S$  and the centre  $C$ . How to “extract” such true molecular information from experimental values of activation energy is a field of interest of the SET model.

What type of reservoirs of energy can be considered in the reacting system? If we consider the molecular system isolated from environment we must add to it a source of energy as a model representation of the reservoir containing the necessary number of appropriate energy quanta (as it is in an ECS model [9,10] of catalytic molecular devices). If we will consider the molecular catalytic system immersed in a large chemical system we can use the idea of heat bath (as it is in SET model [2] where number and type of energy quanta are not limited). Appropriate relations between the source of energy (molecular scale) and the heat bath (macroscopic scale) can usually be found in each of the particular cases of the considered reaction systems. For instance, if the vibrational mode resulting from SET calculation is a mode characteristic also for the catalyst, the physical character of the source of energy can be conceived as the microenvironment (the nearest appropriate vibrators in catalyst) of a single catalytic centre. Alternatively, if SET predicts as the source of energy a vibrational mode of other molecules of the reactant  $S$ , these molecules are probably present in large excess in gas or liquid phase.

The process of activation of the reactant molecule  $S$  can be treated as a single event or as a sequence of consecutive elementary events. This raises the important question: is a case when the catalytic system needs only one quantum jump better than a case when the system needs many energy quanta? The above-mentioned compensation effect and/or comparison between heterogeneous and enzyme catalysts for the same reaction indicate that the answer is not trivial. Notice that in all cases the events are physical rather than chemical events-excluding the last jump to the top.

Just at that moment, when the top of necessary activation has been reached the energy requirement for the catalytic reaction to occur is fulfilled. At that moment, simultaneously, the condition of synchronisation of the best electron density distribution in the reactant  $S$  and in the centre  $C$  must be operating. If so, the reaction occurs.

## 6. Regions of applicability of SET and IOM

SET was introduced for explanation of isokinetic effect; until now it has been used mainly in heterogeneous catalysis. There is, however, no reasons that Eq. (1) should not hold also for homogenous, (e.g. [13]) and or enzyme reaction systems. In this connection one encounters the problem of the lowest possible activation energy for a reaction. One can observe that if the geometrical conditions are such that deformation of the co-ordinate is not needed, there is no need to excite the potential curve and hence the activation energy should be zero. Such conditions can be said to be met in most cases for the reaction  $H_2 + M + M \Rightarrow M-H + M-H$  that falls into category if the metal is regarded as the catalyst as well as the reactant. Similarly if geometric conditions are such that just a very little deformation is required for reaction, only one or just a few vibrational levels have to be excited.

It must be stressed that the principles of the SET model are not limited to reactions showing isokinetic effect as the Eq. (1) is a very general one. It treats also stepwise change of activation energy [6].

IOM is likewise applicable [3,9,10] to both homogeneous, heterogeneous as well as enzyme catalysis. The computed time parameters (vibrational periods)

contain also information on energy, chemical composition and geometry of the selected vibrators in the reacting system. In particular, the values of shift of the calculated frequencies in the system in comparison to these frequencies of the reactant *S* and of the centre *C* out of the system (available from experimental spectroscopic data) one can use in analysis of the geometry requirements in the system. The simplest example of such approach can be the use of well-known shifts of a metal-ligand stretching mode frequency depending on geometry of metal complex used as a homogeneous catalyst. We suggest that the shifts of the frequencies resulting from comparison of the calculated with the SET and IOM models frequencies and ones for non-interacting reactant and catalytic centre can serve as the base data in choice of the real systems for quantum chemistry calculation.

## 7. Selectivity

At molecular level selectivity can be defined as a choice of one (let us say A) from two possible paths (path A and B) which is made by a single molecule of reactant. Notice that at the molecular level a statement that a molecule will go along path A with probability, e.g. 40% has no physical sense, in contrast to consideration of a big set of the molecules. If a single molecule can go along path A or along path B depends on particular molecular conditions just at the moment of making the choice. We can only ask what are the conditions and what is a probability of appearance of these conditions in a considered system.

According to SET model the choice is determined by the activation of the crucial mode of reactant (for instance, in the reaction of decomposition of HCOOH: if at the moment of making the choice OCO bending mode is activated the reaction run via dehydrogenation path, while dehydration path is chosen if OCO asymmetric stretching mode is enough activated). In other words, selectivity of reaction depends on selectivity of energy transfer. From the point of view of time requirements (IOM) single molecule of reactant will go along that path for which the time of synchronisation is shorter. Therefore, we can point out that, in our description at molecular level, selectivity is determined simultaneously by the two following condi-

tions: selective activation of crucial mode(s) and synchronisation of well-defined favourable distribution of electron density in reactant and catalytic centre.

In order to discuss probability of appearance of these conditions let us consider a real catalytic reaction system, e.g. the decomposition of formic acid on a heterogeneous catalyst, where a number of side-reactions and the two main (dehydrogenation and dehydration) reactions can occur. According to our previous results [5–7] selectivity of decomposition of HCOOH towards the dehydrogenation reaction depends on selective activation of the OCO bending mode (SET model) and on appropriate ranges of wavenumbers of the mode in formate ion adsorbed as bidentate species and of the stretching mode of hydroxyl group on the catalyst surface. In these selected ranges time of synchronisation (IOM) for the dehydrogenation reaction is shorter than the time for dehydration reaction. Taking into account others optimal ranges of formate ion internal vibrational modes and of potential catalysts (metal-oxygen stretching mode) one can find the optimal conditions for the dehydrogenation reaction. In particular, one can find appropriate molecular properties of catalytic centres that fulfilled simultaneously SET and IOM conditions. For instance, in the SET calculation it was found [6] the value  $765\text{ cm}^{-1}$  for the OCO bending mode, and in the IOM calculation [7] the optimal range of wavenumbers for the synchronisation for the same mode is  $760\text{--}720\text{ cm}^{-1}$  for one of the potential catalyst ( $750\text{--}720\text{ cm}^{-1}$  for metal-oxygen stretching mode assigned to  $\text{TiO}_2$ ) and  $3500\text{--}3460\text{ cm}^{-1}$  or  $3260\text{--}3200\text{ cm}^{-1}$  for the surface hydroxyl group adjacent to the bidentate species of adsorbed formate ion.

According to our approach, if one can obtain a catalyst with a high population of active sites with such molecular properties, the catalyst should be highly selective towards the dehydrogenation reaction.

The side-reactions occurring in the assumed reaction system must be caused by different selective activation and different optimal ranges of wavenumbers. The probabilities of the occurrences of these reactions depend on the proportion of available energy source vibrators in relation to energy vibrators desired for dehydrogenation and/or dehydration reactions, i.e. distribution of the necessary molecular properties of centres in relation to molecular properties useful for the main reactions.

## 8. Activity

In practice, activity of a single site of catalyst is expressed by the turnover number or turnover frequency, obtained from experimental macroscopic activity of the catalyst divided by the estimated number of active sites of the catalyst. Note that in this way a mean value of the site is obtained as one assumes that all the sites are equally active. In order to predict the activity of a catalyst from first principles, however, one must know about the distribution of the site activity among available sites.

An example might illustrate this. Hydrogen peroxide decomposition on catalase has a turnover frequency of about  $10^5$  mol  $\text{H}_2\text{O}_2$ /mol catalase/s. Let us assume that using an inorganic catalyst, e.g. ferrous hydroxide, the major part of the sites have a turnover of about  $10^{-5}$ , but that there are some few sites with an activity equalling that of catalase. Hence the presence of only  $10^{-9}$  mol of these sites/mol of the hydroxide catalyst would give a catalyst with a resulting activity of  $10^{-4}$ , 10 times higher than what had been the case otherwise.

In our approach to design new catalysts we start from molecular level properties (vibrational frequencies and catalyst bond lengths) and combine the outcome with information on distribution of these properties in the catalyst system.

In the physical model presented above the elementary catalytic act is treated as a sequence of the two types of events, namely activation of reactant (and/or of centre) and the synchronisation of the favourable distribution of electron density in reacting system. Therefore, the time of the catalytic act, measured from the moment of creation of the reacting system to the moment of appearance of product, is the sum of the time of activation and of the time of synchronisation.

The time of activation (as described by SET) is determined by the possibility of good resonance between vibrators and also by the structure of the interaction of reactant and catalyst. This will determine how many quanta of the vibrational mode that must be excited. Hence one should describe the distribution of vibrators with “correct” frequency in the catalyst and also the distribution of suitable bond lengths.

In the IOM model the time of synchronisation is calculated with the assumption that energy and geometry requirements are fulfilled. We suggest that the short-

est time of the synchronisation represents the most active catalytic centre. Thus, there exists a close relation between molecular vibrations and the activity at the molecular level. To find the best catalyst one must also in this case describe the distribution of sites with such molecular vibrations.

## 9. Concluding remarks

Based on the common physical model we suggest treating the SET and IOM as complementary descriptions of the energy and time requirements of the catalytic act. From these descriptions we can have information on molecular level properties of the catalytic system. In particular, we obtain the set of calculated frequencies of the selected vibrational modes in the “ideal” best molecular catalytic system. It seems that the geometry requirements result from the energy and time requirements.

There are at least two possible ways to transform the obtained set of frequencies into real catalytic systems, i.e. to develop computer-aided design of new improved catalysts. The simplest way seems to be the use of experimental spectroscopy databases as well as to make auxiliary quantum chemistry calculations for simplify potential catalytic systems for which the experimental data are not available. We have studied in this way systematically [14–20] the reacting systems that are in our field of interest.

The second way is the application of quantum chemistry calculations when one would develop a procedure using our suggestion that the shifts of the frequencies resulting from comparison of the calculated with the SET and IOM models frequencies and ones for non-interacting reactant and catalytic centre can serve as the base data in choice of the real systems for ab initio quantum chemistry calculation. We have started to develop this way. The simplest example of such approach can be the use of well-known shifts of a metal-ligand stretching mode frequency depending on geometry of metal complex used as a homogeneous catalyst. One can also try to correlate the different co-ordination structure with the metal-ligand bonds length changes predicted by the SET. More systematic experimental and theoretical studies on the strong solvent effect from the point of view of the approach presented in this paper should be developed.

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