

# On the physical nature of the so-called vibropolaritonic chemistry

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## Abstract

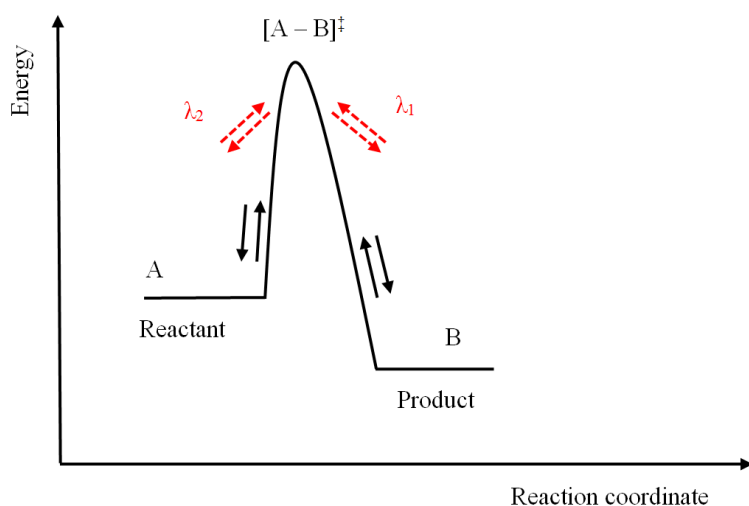
The phenomenon of vibropolaritonic chemistry is that a chemical reaction inside a Fabry-Perot cavity can speed up, slow down, or change direction. Despite intensive theoretical and experimental study of this phenomenon, its physical nature remains unclear. We offer a physical explanation of the nature of the phenomenon, taking into account the fundamental property of quantum physics - its time reversal noninvariance.

**Keywords:** vibrational strong coupling, vibropolaritonic chemistry, Fabry-Perot resonator, time reversal noninvariance.

It was probably discovered for the first time in work [1] that if a chemical reaction is carried out inside a Fabry-Perot resonator, its rate can change. This phenomenon aroused great interest of chemists and physicists. To date, a large number of experimental [2-8] and theoretical [9-15] studies have been carried out. Phenomenological models and mathematical descriptions of the phenomenon are proposed. However, there is still no clear physical explanation of the nature of the phenomenon. Here we offer such a physical explanation.

From a physical point of view, the Fabry-Perot resonator is a battery, a storage of photons of a certain wavelength. These photons influence the course of the chemical reaction. Where do photons come from there? How can they influence a chemical reaction when, in order to overcome the activation barrier, a molecule usually has to absorb a large number of infrared photons [16]? However, such an influence is possible.

As an example, consider the reactive landscape shown in Figure 1 for the simplest variant of a monomolecular isomerization reaction. Reagent A is converted to product B. There is a potential energy barrier between them. The molecule receives energy to overcome this barrier when it collides with other molecules (solid arrows) and goes into the transition state complex  $[A-B]^{\ddagger}$ . For some time, the molecule exists in the state of the transition complex, where it changes its structure. Further, as a result of the loss of part of the energy, this structure is stabilized in the form of a product or in the form of an initial compound. Excess energy can be lost in the same collisions.



**Fig. 1** Reactive landscape for a monomolecular isomerization reaction.

Since the molecules in the transition state are relatively highly excited, their vibrational states are populated. Accordingly, they can also lose energy as a result of spontaneous or stimulated emission of IR photons. This is a variant of radiation stabilization of the transition state (red dotted arrows). These photons accumulate in the Fabry-Perot resonator.

Spontaneous or stimulated emission of photons by the transition complex is the so-called forward process. After the photon is emitted, the molecule can absorb the same or similar photon. This process is called reversed to the initial state.

So, forward and reversed processes in quantum physics are nonequivalent. In other words, this is called - time reversal noninvariance. We have more than enough direct and indirect experimental evidence of this nonequivalence [17]. The difference between the differential cross sections of forward and reversed quantum processes can be many orders of magnitude. Therefore, a reversed quantum process can be much more efficient than a forward process. This means that the radiation channel for the stabilization of the transition state under the conditions of the Fabry-Perot resonator can be blocked. If the blocking of the stabilization of the transition state occurs towards the reaction product ( $\lambda_1$ ), then a slowdown in the chemical reaction will be observed. If such blocking occurs in the direction of the initial reagent ( $\lambda_2$ ), then an acceleration of the chemical reaction will be observed.

In fact, such blocking is a complete phenomenological analogue of the quantum Zeno effect, which is widely known in quantum physics. There, frequent measurements prevent the decay of the quantum system [18]. The real situation there is slightly different: "measurements" help return the quantum system to its initial state and some "refresh" its memory [19]. But there are details.

Thus, there are few photons in the Fabry-Perot resonator. They are emitted by the molecules themselves. The Fabry-Perot resonator only holds them and facilitates the process of

returning the molecules to the initial state of the transition complex. This means blocking the radiation stabilization channel of the transition complex in one state or another. It is clear that in order to change the rate of a chemical reaction in this case, the molecule does not need to absorb many IR photons. One is enough.

### Conclusion

Excited molecules of the transition complex emit IR photons, which are held in the Fabry- Perot resonator. Due to the high efficiency of the reversed quantum process to the initial state of the quantum system, the process of radiation stabilization of the transition complex is blocked and the chemical reaction is accelerated or slowed down. In fact, such blocking looks like as a full analogue of the quantum Zeno effect.

The discussed mechanism needs further study and verification. In our opinion, experiments with input of external IR radiation with different intensity, wavelength and spectral width into the Fabry-Perot resonator are of interest.

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