Introduction

The atmosphere can be considered as a large chemical reactor in which various type of reaction can occur. As it was shown the peroxy radicals are a significant intermediers in the chemical process of the troposphere at both, polluted and clean environment. In the polluted environment the role of the peroxy radicals are clear, lots of experimental and quantum chemical results are available about this. But the reaction channels in the clean environment is much less known. There is the question at low NO_x concentration, when the self- and cross reactions become predominant, if RO_2 radicals could also react with the OH radical, i.e., there is a possibility that under these conditions OH radicals do not react only with hydrocarbons, but possibly also with peroxy radicals. However, there are no experimental or theoretical data in the literature about any RO_2 + OH reaction, so it is not a surprise, that this reaction is not included in the atmospheric chemistry models. The investigation is started with the reaction between the smallest peroxy radicals, CH_3O_2, and OH radicals. Our main goal was studying the RO_2 + OH reaction family and understanding its role in the chemistry of troposphere.

The absorption spectrum for the CH_3O_2 radicals has been measured several times in the near IR region[66,67,70]. A first report on the absorption features of peroxy radicals in the near infrared was given in 1976 by Hunziker and Wendt using a modulated formation of peroxy radicals[70]. Later the spectrum has been published again by Pushkarsky et al.[67] using pulsed cavity ring down spectroscopy (CRDS) coupled to laser photolysis. Pushkarsky et al. used a Raman shifted dye laser for generating the near IR radiation and were therefore able to cover a wide wavelength range (7300 – 7700 cm^{-1}). They have located the 0-0 transition at 7382.8 cm^{-1} and have obtained an absolute absorption cross section of $(2.7 \pm 1.4) \times 10^{-20}$ cm^2. A few years after Pushkarsky et al., the spectrum of the CH_3O_2 radical was again measured by Atkinson and Spillman[66], demonstrating for the first time the coupling of continuous wave-CRDS to laser photolysis. They located its maximum at 7490.24 cm^{-1} (compared to 7488 cm^{-1} for Pushkarsky et al.) and reported an absorption cross section of $\sigma = (1.5 \pm 0.8) \times 10^{-20}$ cm^2 molecule^{-1}. For obtaining the absorption cross section of this radical, both groups have used the same method: measuring the time resolved CH_3O_2 decays and taking advantage of the known rate constant for the self-reaction of CH_3O_2 radicals in order to deduce the initial CH_3O_2 concentration.

	Peaks of the absorption spectrum in the near-IR region	Absorption cross section
Atkinson[66]	7490.2 cm^{-1}	$(1.5 \pm 0.8) \times 10^{-20}$ cm^2
Miller[67]	7490.4 cm^{-1} 7488.0 cm^{-1} 7382.8 cm^{-1}	1.1×10^{-20} cm^2 1.1×10^{-20} cm^2 2.7×10^{-20} cm^2

Table 1 : *The relevant literature data about the* CH$_3$O$_2$ *absorption cross section and maximum of its absorption spectrum in the IR-region*
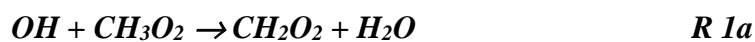
So there is a given disagreement in the literature in connection of the absorption spectrum and absorption cross section of CH$_3$O$_2$ radical.

Reaction CH$_3$O$_2$ + OH is a radical-radical recombination reaction of which description is a real challenge both experimentally and theoretically. In the literature only a few paper can be found which studies similar systems, but they use mostly lower level of theory calculations[87,89,91,93,108]. Considering the theoretical investigation of the reaction CH$_3$O$_2$ + OH, mostly calculations for CH$_3$O$_2$ + OH model systems can be found in the literature. Du and Zhang[6] determined the singlet or the triplet potential energy surfaces of the CF$_3$O$_2$ + OH system at B3LYP/6-311G(d,p) level of theory. CF$_3$O and HO$_2$ found as the predominant products.

The CH$_3$O$_2$ + OH reaction occurred also in the modeling study of Burkert *et al.*[7] as the part of the reaction scheme of CH$_4$ + CO system. They found that the products are mostly methanol, CH$_3$OH and singlet oxygen molecule. Furthermore, they have given an estimation of the rate constant of the title reaction, 1×10^{-10} cm^{3}molecule^{-1}s^{-1}, which was based on the rate coefficient of HO$_2$ + OH reaction measured by Tsang and Hampson[8].

The CH$_3$O$_2$ + halogen reactions can be used as proxy for the CH$_3$O$_2$ + OH reaction. For this type of reaction only experimental study can be found in literature. Most of the studies agree that the two main channels are the hydrogen abstraction and the oxygen atom transfer[9–11], i.e., the products are possibly methoxy, CH$_3$O, or CH$_2$O$_2$, Criegee radical. The global rate constant is around 2×10^{-10} cm^{3}molecule^{-1}s^{-1} which shows that the title reaction must be also similarly fast.

In a recent modeling study, Archibald and co-workers[85] have investigated the impact of including the reaction between RO$_2$ and OH on the composition of the Marine Boundary Layer (MBL). They have run different scenarios using a model named BAMBO, based on the master chemical mechanism (MCM) mechanism[86]. Different possible reaction paths were simulated for peroxy radicals up to C4, leading for the simplest one, CH$_3$O$_2$, to the following products:

$$OH + CH_3O_2 \rightarrow CH_2O_2 + H_2O \qquad\qquad \textbf{R 1a}$$

$$\rightarrow CH_3O + HO_2 \qquad\qquad \textbf{R 1b}$$

$$\rightarrow CH_3OH + O_2 \qquad\qquad \textbf{R 1c}$$

For all scenarios they found only a small, negligible effect on the mixing ratios of O_3, NO_x, OH and other trace gas species in the marine boundary layer. However, a substantial increase in the mixing ratios of HCOOH was observed (from 0.16 ppt in the base case, *i.e.* absence of OH + $CH_3O_2 \rightarrow CH_2O_2 + H_2O$ R 1, to 25.5 ppt), if the reaction pathway would be formation of the Criegee radical $OH + CH_3O_2 \rightarrow CH_2O_2 + H_2O$ R 1a. A strong increase in the mixing ratio of CH_3OH (from 37 ppt in the base case, i.e. absence of $OH + CH_3O_2 \rightarrow CH_2O_2 + H_2O$ R 1 to 294 ppt), was observed if the major pathway would be $OH + CH_3O_2 \rightarrow CH_2O_2 + H_2O$ R 1c. The impact on the RO_2 and HO_2 radical budget was below 10 % for all scenarios.

Since higher level calculations were planned to determine the PES of CH_3O_2 + OH as exact as possible. First, a method test was carried out, where a smaller test system, $CH_3 + HO_2$ was used. The reaction channels were the followings.

The complete reaction mechanism is summarized in **Scheme I**.
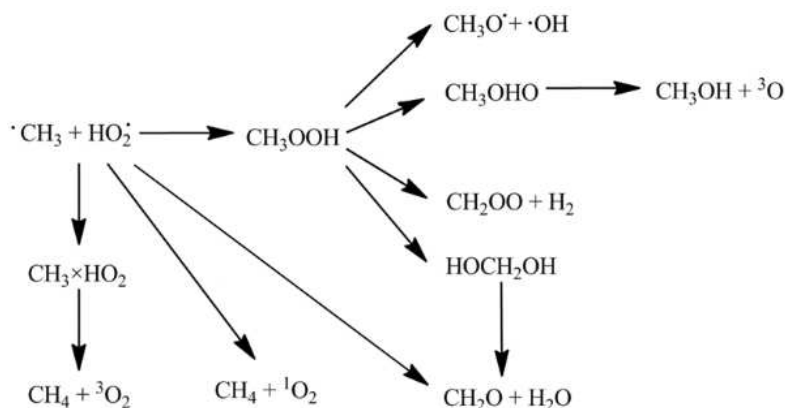
Scheme 1: **The detailed outline of the $CH_3 + HO_2$ reaction system.**

In this work, a newly-developed, HEAT345-(Q)-based high-level *ab initio* method called CHEAT1 will be introduced whilst computing the potential energy surface of the $CH_3 + HO_2$ reaction system. This will provide a general, single-reference based accurate description of this system, and yield reliable information for kinetic modeling. However, the calculation of overall rate constant is omitted, since these results can be sensitive to the combination of the rate theories used for the kinetic modeling.

Methods and Results

I.   *The CH₃O₂ and CH₃I absorption spectrum has been measured in the wavelength range 7497.4 – 7473.8 cm⁻¹ at a total pressure of 50 Torr helium. The absorption cross section of CH₃O₂ radical was determined at the three peaks at 50 and 100 Torr pressure.*

The two spectra were measured by continuous wave cavity ring-down spectroscopy (cw-CRDS) in the near IR region in a house made fast flow system. In the both cases $\tilde{B} \leftarrow \tilde{X}$ transition was used for detection. The measured absorption spectra are depicted in Figure 1. The absorption cross section summarized in Table 2 was determined at the three large peaks found in the spectrum of the CH_3O_2 radical.
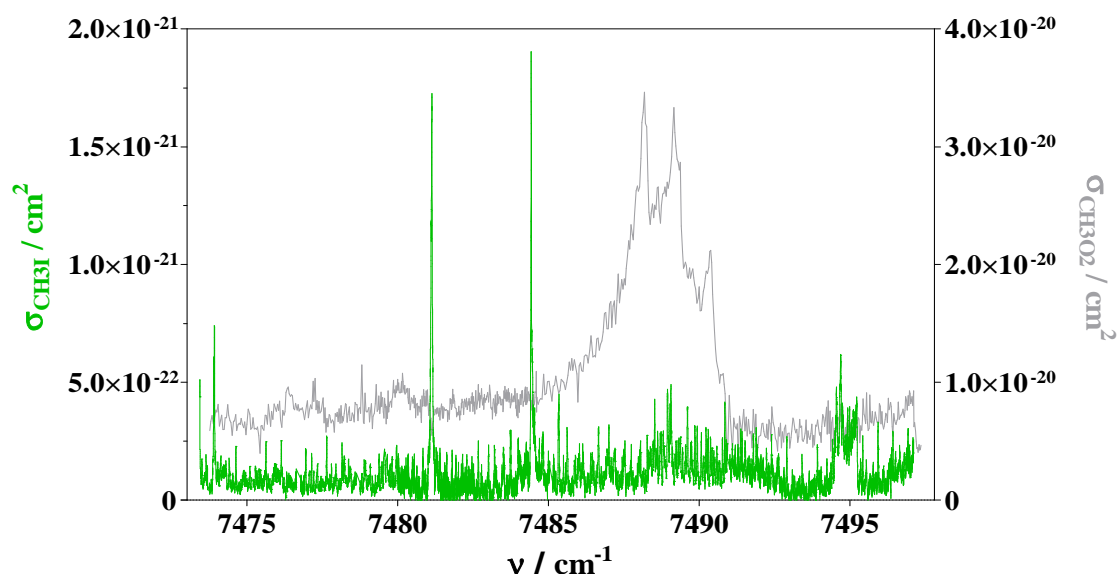

Figure 1: **Full absorption spectrum of CH₃I (green line, left y-axis) and CH₃O₂ (grey line, right y-axis).**

The absorption cross section does not depend on the pressure between 50 and 100 Torr but as it is expected different values were measured at different peaks.

ν / cm⁻¹	$\alpha_{\text{full spectrum}}$ / cm⁻¹	$\sigma_{CH_3O_2,\text{50 Torr}}$ / 10^{-20} cm²	$\sigma_{CH_3O_2,\text{100 Torr}}$ / 10^{-20} cm²
7488.18	$(4.38\pm0.3) \times 10^{-7}$	3.43 ± 0.21	3.39 ± 0.04
7489.16	$(4.22\pm0.3) \times 10^{-7}$	3.37 ± 0.12	3.42 ± 0.05
7490.33	$(2.67\pm0.3) \times 10^{-7}$	2.13 ± 0.09	2.12 ± 0.05

Table 2 : **Summary of absorption coefficients from full spectrum and absorption cross section from kinetic measurements.**

II.   A new composite method (CHEAT1) was introduced which was tested on a small radical-radical reaction system (HO₂ + CH₃). The potential energy surface was determined byusing of CHEAT1 method. The results proved that the CHEAT1 protocol is accurate enough and perfectly applicable method for description of radical-radical reactions.

The simplified HEAT345-(Q) (CHEAT1) protocol's performance demonstrates that it provides a comprehensive, robust and highly accurate theoretical description of the system studied. Since the CCSDT(Q)/cc-pVDZ level of theory is included in the CHEAT1 protocol, no multi-reference treatment of the system is needed for the proper description of the higher excitations.

III.   Using the CHEAT1, three new, low-lying channels were described in the test system (CH₃ + HO₂ reaction which is very similar to the RO₂ + OH type reaction.

Based on our combined theoretical method, three new low-lying reaction channels have been characterized. The triplet oxygen atom and methanol can be formed by a two-step mechanism involving H-shift of CH_3OOH and intersystem crossing of methanol oxide. Indirect water elimination *via* methylene glycol was also identified. Finally, molecular hydrogen elimination can result in the formation of methylene peroxide. The potential energy surface (PES) of reaction $CH_3 + HO_2$ is depicted in Figure 2.
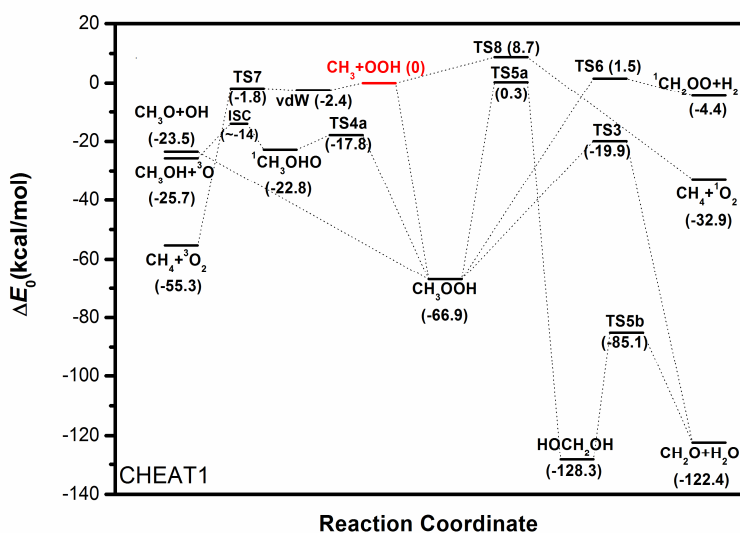
Figure 2: The potential energy diagram of CH₃ + HO₂ reaction system calculated by the CHEAT1 protocol.

IV.   *The rate constant of the reaction between the methylperoxy radical CH₃O₂, and the OH radical has been measured for the first time which is $(2.8 \pm 1.4) \times 10^{-10}$ cm³s⁻¹.*

Relative OH decays have been obtained by high repetition rate LIF in the presence of excess CH_3O_2. The absolute concentration of CH_3O_2 was measured simultaneously by time resolved cw-CRDS in the near IR. A very fast rate constant of $(2.8 \pm 1.4) \times 10^{-10}$ cm³s⁻¹, independent of pressure between 50 and 100 Torr, has been obtained. With such a fast rate constant, the reaction of CH_3O_2 radicals (and peroxy radicals in general) with OH radicals will be needed to be implemented into atmospheric chemistry models, as it will have non-negligible impact on the composition of the atmosphere especially in remote environments where NO_x concentrations are low and the lifetime of peroxy radicals is long.

V.   *The results of the PES determination of CH₃O₂ + OH reaction at G4 and CBS-APNO level of theory were those the products of the most favorable channel are CH₃O and HO₂ radicals, and the reaction is barrierless.*

First, the termodynamical control of the reaction was determined. The isomers of CH_4O_3 structure were calculated at G3MP2B3 level of theory. Then at two levels of theory, G4 and CBS-APNO were used for determination of the PES (depicted in Figure 3) which was very complicated due to the cross points between the singlet and triplet surface. At every TS structure IRC calculations were carried out to validate the assumed pathway. Most of the cases the first step is a barrierless addition of the CH_3O_2 and OH. Then the most favorable channel ends at $CH_3O + HO_2$ since this is accordingly also a barrierless process, no TS was found only a vdW complex can be obtained. The data obtained from the two different methods show good agreement each other.
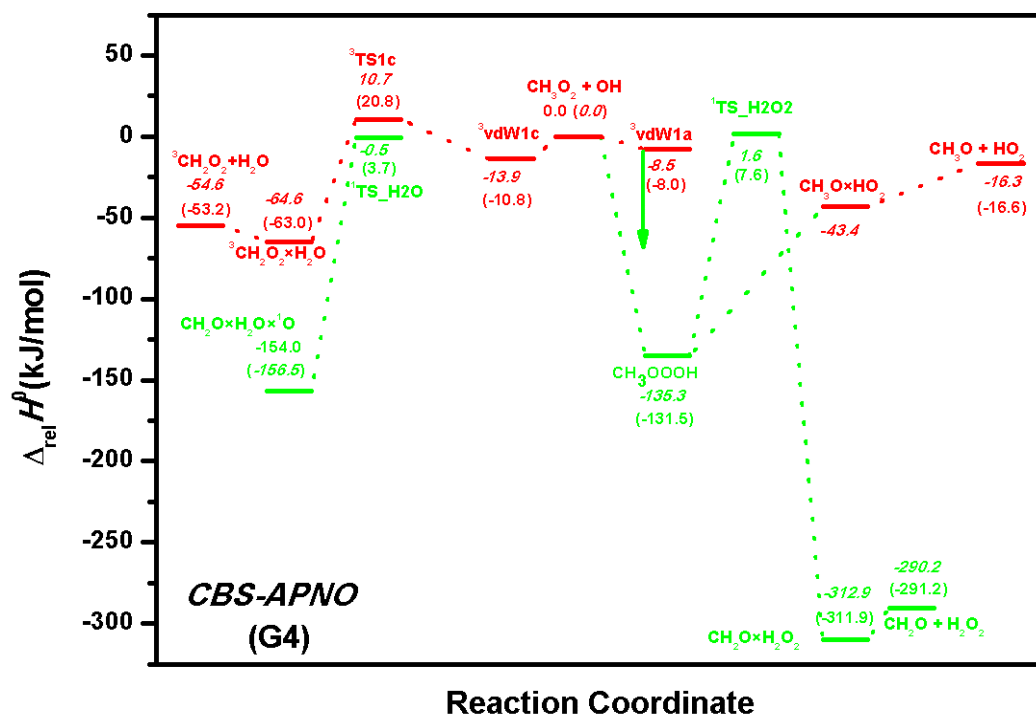
Figure 3: **The enthalpy profile of CH$_3$O$_2$ + OH reaction. The red elements are on the triplet surface while the green ones are on the singlet surface. The enthalpy values written in the graph are calculated at two level of theory, *CBS-APNO* and (G4).**

VI. *Measuring the rate constant of the reaction of ethyl peroxy radicals, C$_2$H$_5$O$_2$ and OH radicals for the first time, which is (1.2 ± 0.3) × 10^{-10} cm^{3}s^{-1}.*

OH decays were followed under pseudo-first order conditions in the presence of excess C$_2$H$_5$O$_2$ radicals by laser induced fluorescence (LIF) technique. C$_2$H$_5$O$_2$ radicals were generated from Cl-atoms in the presence of C$_2$H$_6$ / O$_2$, whereby the concentration of Cl-atoms was determined prior to each experiment by conversion to HO$_2$, quantifiable by cw-CRDS in the near-IR region. A fast rate constant of k = (1.2 ± 0.3) × 10^{-10} cm^{3}s^{-1} was observed at 50 Torr, showing that the reaction of C$_2$H$_5$O$_2$ + OH plays some role as sink for C$_2$H$_5$O$_2$ radicals in remote environments and needs to be integrated in atmospheric chemistry models.

VII. *We determined the potential energy surface of reaction $C_2H_5O_2$ and OH at CBS-APNO level of theory. It was found that the most favorable channel ends at $C_2H_5O + HO_2$ since this is accordingly also a barrierless process.*

In order to have a first guess about the PES, the isomers of $C_2H_6O_3$ structure were calculated at G3MP2B3 level of theory. Then CBS-APNO level of theory was used for further calculation and determination of the potential energy surface, which was very complicated due to the cross points between the singlet and triplet surface. Most of the cases the first step is a barrierless addition of the CH_3O_2 and OH. Then the most favorable channel ends at $C_2H_5O + HO_2$ since this is accordingly also a barrierless process, no TS was found only a vdW complex can be obtained.
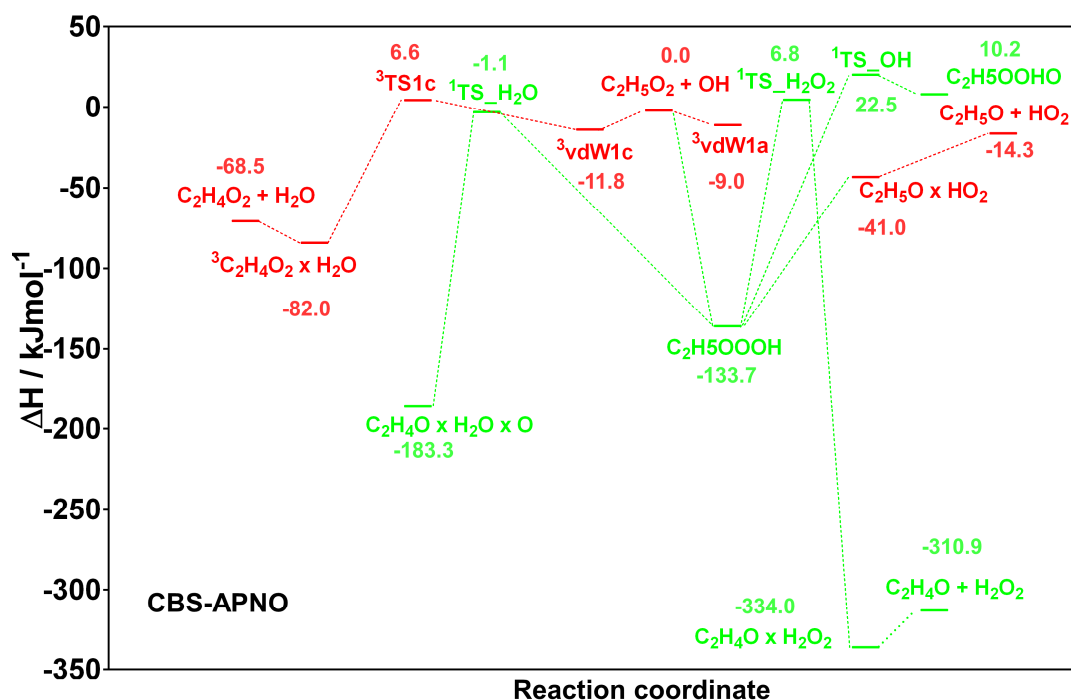

Figure 4: **The enthalpy profile of $C_2H_5O_2$ + OH reaction. The red elements are on the triplet surface while the green ones are on the singlet surface. The enthalpy values written in the graph are calculated at *CBS-APNO* level of theory.**

Publications

Related to the dissertation

  (1) **Faragó P., Eszter**; Szőri, Milán; Owen, Michael C.; Fittschen, Christa; Viskolcz, Béla; Critical evaluation of potential energy surface of the CH_3+HO_2 reaction system *J. Chem. Phys., 142 (5)*, 054308, **2015**. **IF:3.12**

  (2) **Faragó P., Eszter**; Schoemaecker, Coralie; Viskolcz, Béla; Fittschen, Christa; Experimental determination of the rate constant of the reaction between $C_2H_5O_2$ and OH radicals *Chem. Phys. Lett.*, *619*, 196-200, **2015**. **IF:1.99**

  (3) Bossolasco, Adriana; **Faragó P., Eszter**; Schoemaecker, Coralie; Fittschen, Christa; Rate constant of the reaction between CH_3O_2 and OH radicals *Chem. Phys. Lett.*, *593* (0), 7-13, **2014**. **IF: 1.99**

  (4) **Faragó P., Eszter**; Viskolcz, Béla; Schoemaecker, Coralie; Fittschen, Christa; Absorption Spectrum and Absolute Absorption Cross Sections of CH_3O_2 Radicals and CH_3I Molecules in the Wavelength Range $7473 – 7497$ cm^{-1} *J. Phys. Chem. A*, 117 (48), 12802–12811, **2013**. **IF:2.77**

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Other publications:

  (1) Szórád, János J.; **Faragó P.,** Eszter; Rágyanszki, Anita; Cimino, Franco A.; Fiser, Béla; Owen, Michael C.; Jójárt, Balázs; Morgado, Claudio A.; Szőri, Milán; Jensen, Svend J. Knak; Csizmadia, Imre G.; Viskolcz, Béla; Conformation change of opiorphin derivatives. A theoretical study of the radical initiated epimerization of opiorphin *Chem. Phys. Lett.*, DOI:10.1016/j.cplett.2015.03.008 **IF:1.99**

  (2) Hegedüs, Imre; **Faragó, Eszter**; Kálmán, Mihály; Nagy, Endre; Biomedical applications of single protein nanoparticles, *Journal of Pharmacy and Pharmacology*, 2, 652-659, **2014. IF:2.26**

  (3) Lam, Audrey T.; **Faragó P.,** Eszter; Owen, Michael C.; Fiser, Béla; Jójárt, Balázs; Jensen, Svend J. Knak; Csizmadia, Imre G.; Viskolcz, Béla; The effect of oxidative stress on bursopentine peptide structure: a theoretical study *Phys. Chem. Chem. Phys.*, *16(20),* 9602-9609, **2014**. **IF:3.20**

  (4) Hegedüs, Imre; **Faragó, Eszter**; Kálmán, Mihály; Nagy, Endre; Biomedical applications of single protein nanoparticles: drug delivery through the blood-brain barrier, *Technical Review (EMT)*, 14(56), 10-20, **2011**. **IF:0.79**

<p align="center">Cumulative impact of supplemented journal articles: 8.24</p>