

# On the applicability of MP2.5 method in atmospheric reactivity

Siba Suleiman, Michal Novotný and Ivan Černušák

*Comenius University in Bratislava, Faculty of Natural Sciences, Department of physical and theoretical chemistry, Ilkovičova 6, 842 15 Bratislava, Slovak republic;  
sibs.suleiman@gmail.com*

## Abstract

Quantum chemical study has been performed on the reaction energies of the reactions of methyl iodide  $\text{CH}_3\text{I}$  and di-iodomethane  $\text{CH}_2\text{I}_2$  with hydroxide radical. Both series of reactions were treated using the following methods: MP2, MP3, CCSD, CCSD(T) and also with the so-called MP2.5 approximation which is expected to be a good approximation to CCSD(T) within either chemical ( $\pm 4\text{kJ/mol}$ ) or sub-chemical accuracy ( $\pm 10\text{kJ/mol}$ ). We have used the correlation consistent cc-pvtz basis set in all calculations. In these atmospheric reactions, we considered various types of products. These reactions represent either isogyric processes or processes leading to atomic species. When comparing the MP2.5 and CCSD(T) data for reaction energies, our results indicate that there are some differences in reaction energies when the reaction contains different number of radicals and/or atoms on both sides. In addition, all the reactions including IO species do not fit into the “MP2.5 computational philosophy”.

**Keywords:** *atmospheric chemistry; reaction energy; perturbation theory; coupled cluster; iodine*

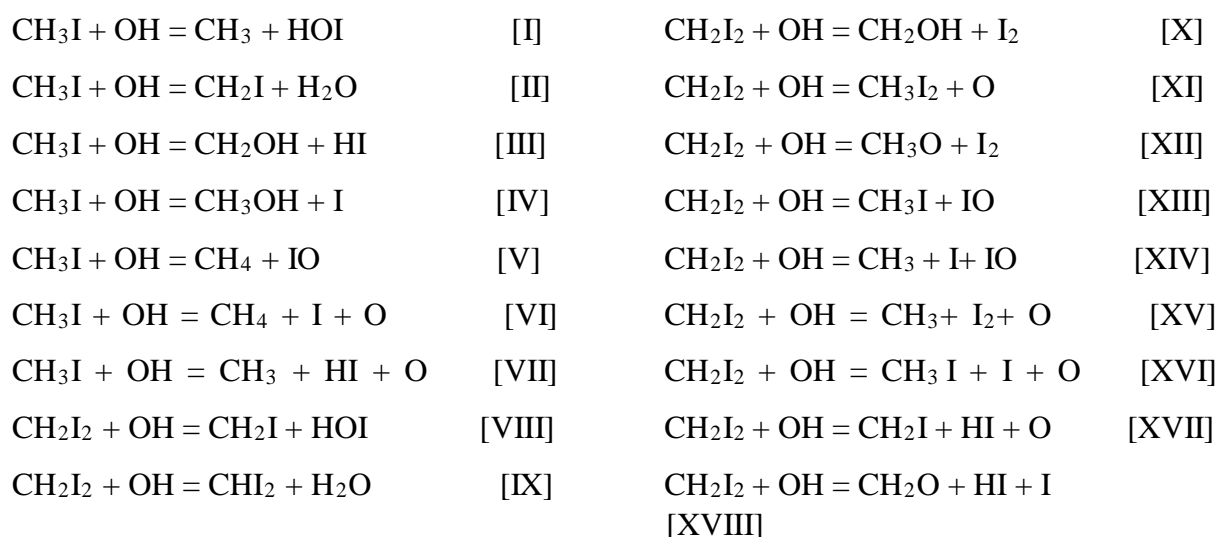
## Introduction

Iodine is a very important element in the atmosphere and his importance is known for more than two decades [1]. Among the frequently discussed effects of atmospheric iodine are: (i) the ozone depletion in the lower stratosphere and due to the presence of IO, (ii) the role of iodine compounds in new particle formation in marine environments, (iii) chemistry of halogens in troposphere through the interaction of iodine compounds with bromides and chlorides.

There are several other organic compounds besides iodomethane ( $\text{CH}_3\text{I}$ ), e.g.,  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{CII}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{C}_3\text{H}_7\text{I}$ . These species have been detected in marine boundary layer in the coastal water or in open ocean [2]. Iodomethane and di-iodomethane are mostly produced by microalgae and phytoplankton in marine boundary layer and belong to the most abundant and reactive alkyl iodides in the troposphere [3]. These compounds can undergo several decomposition pathways. For instance,  $\text{CH}_3\text{I}$  is easily photolyzed giving iodine atoms. As known, iodine can enter ozone cycle or can react with NO,  $\text{HO}_2$ , ClO, BrO, or IO. Also,  $\text{CH}_3\text{I}$  can abstract either H or I under attack of active oxidizing agent - OH radical.

High-level ab initio molecular orbital studies offer a viable alternative to provide reliable thermodynamic and kinetic data for the gas-phase chemical reactions. Modelling H- or I-abstraction from alkyl iodides is rather demanding task. It is desirable to reach the chemical accuracy of the underlying thermodynamic data (better than  $\pm 4$  kJ/mol) that can be used in subsequent thermochemical modelling. This implies to choose the computational chemistry tools that include all necessary and accurate corrections to molecular energies (basis set saturation, valence and core-valence electron correlation, relativistic effects, spin-adaptation, vibration contributions, and tunnelling corrections). However, when aiming at higher halo-alkanes (starting from C4 chain), the computational demands associated with the coupled cluster calculations are dramatically increasing. While the perturbation calculations scale with  $N^4 \div N^5$  (N being a relative measure of the system size, roughly depends on the number of electrons and number of basis functions), the coupled cluster calculation scales as much as  $N^6 \div N^7$  depending on the how it is implemented.

In this contribution, we report the reaction energies for the following set of equilibria:



Our goal is to test the performance of MP2.5 method for specific set of atmospheric processes with the aim to apply it to study the reactivity of higher halogenated hydrocarbons. Specific class of this processes represent *isogyric reactions* in which the number of electron pairs is conserved in participating species.

## Materials and Methods

Theoretical calculations were performed using the Gaussian09 [4] software package. To have all the species represented at consistent computational level, we have re-optimized the geometries of reactants and products using the MP2 and MP3 methods, respectively. This

approach is the post-Hartree–Fock ab initio method of computational chemistry. It improves the Hartree–Fock energy by adding electron correlation effects by means of Rayleigh–Schrödinger perturbation theory to second order. According to Löwdin, correlation energy is defined as the difference between full non-relativistic energy and Hartree-Fock limit [5].

It is known that the geometries referring to stationary points on the MP2 potential energy surface are fairly good and can be utilized in single-point energy calculations with high-level methods, such as coupled clusters CCSD, CCSD(T) methods [5] that work quite well for the systems represented by single Slater determinant. The CCSD method includes the effects of all singly, doubly a part of quadruply excited configurations with respect to the reference Slater determinant. Thus, for the higher-level (CCSD and CCSD(T)) energies we adopted the MP2 geometries. The CCSD(T) approach is nowadays considered in theoretical chemistry as a “golden standard”, providing a relatively good balance between cost and accuracy of the computation on small to medium-sized systems. The difference between CCSD(T) and CCSD represents the effect of triexcitations.

MP2.5 method is based on the observation of the behaviour of the second- and the third order total energies (denoted MP2 and MP3 in the following text). They usually oscillate going from MP2 (too negative contribution of correlation energy) to MP3 (too positive energy). Pitoňák et al. suggested to exploit this property of MP2 and MP3 methods [6] and to evaluate total electronic energy as

$$E(\text{MP2.5}) = E(\text{MP2}) + 0.5 E^{(3)} \quad [1]$$

where  $E^{(3)}$  is the correlation contribution to MP3 total energy of the molecule/atom. We will utilize eq. (1) in the calculation of reaction energies for equilibria [I] – [XVII] and compare them with CCSD and CCSD(T) benchmark data.

## Results and discussion

Tables 1 and 2 contain the values of the energies of the atmospheric reactions which have been calculated in MP2, MP3, MP2.5, CCSD and CCSD(T) approximations with the cc-pvtz basis set. For the comparison of reaction energies of our reactions we can define two sets of quantities: *i*) the difference between MP2.5 and CCSD(T); *ii*) the difference between CCSD and CCSD(T) methods. The former can be used to assess the performance of the MP2.5 approximation, the latter for the indication of the importance of triple-excitation contributions.

**Tab. 1 Reaction energies for the reactions of methyl iodide with hydroxide radical in MP2, MP3, CCSD, CCSD(T) methods with cc-pvtz basis set.**

Reaction	$\Delta E$ (kJ/mol)				
	MP2	MP3	MP2.5	CCSD(T)	CCSD
[I]	-40.2	-62.9	-51.6	-50.0	-55.3
[II]	70.3	50.4	60.4	59.5	55.5
[III]	40.6	24.6	32.6	32.9	30.0
[IV]	415.4	394.3	404.9	397.2	394.0
[V]	-57.0	-57.2	-57.1	-22.5	-30.3
[VI]	61.4	72.1	66.8	65.2	71.6
[VII]	-349.2	-330.1	-339.7	-335.6	-326.6

**Tab. 2 Reaction energies for the reactions of methyl di-iodide with hydroxide radical in MP2, MP3, CCSD, CCSD(T) methods with cc-pvtz basis set.**

Reaction	$\Delta E$ (kJ/mol)				
	MP2	MP3	MP2.5	CCSD(T)	CCSD
[VIII]	86.0	67.2	76.6	78.7	74.0
[IX]	-27.8	-38.6	-33.2	-26.5	-30.7
[X]	88.7	85.7	87.2	86.6	87.0
[XI]	-190.8	-169.1	-180.0	-177.6	-170.2
[XII]	-54.8	-43.8	-49.3	-14.7	-19.8
[XIII]	-50.9	-23.4	-37.1	-1.8	2.4
[XIV]	-301.1	-269.0	-285.1	-282.0	-269.6
[XV]	63.6	85.4	74.5	73.0	82.1
[XVI]	-336.8	-305.8	-321.3	-312.2	-301.9
[XVII]	368.8	358.1	363.5	364.2	362.9
[XVIII]	35.0	55.9	45.4	53.0	57.1

As we can see in [I] – [III] and partly in [VIII] – [X], (isogyric processes), the performance of MP2.5 is very good. For the detailed analysis, see Table 3 for methyl iodide set and Table 4 for di-iodomethane set. As we can see from Tables 3 and 4, when the atmospheric reaction contains IO radical, the difference between MP2 and CCSD(T) methods is rather large. Fig.1 clarifies this situation, indicating that for the remaining equilibria the MP2.5 approximation works quite well, with the errors ranging from chemical to sub-chemical accuracy. The detailed analysis of the excitation amplitudes for IO molecule revealed that in the CCSD

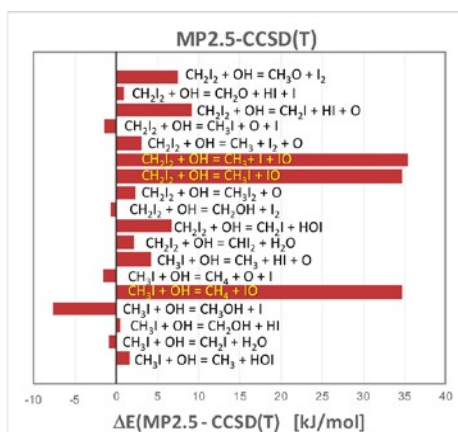
calculation we have one larger bi-excitation amplitude (~0.2 in absolute value). This is the indication of multi-reference character of IO and leads to unacceptable errors visible in Fig. 1.

**Tab. 3** The differences in reaction energy between (MP2.5 - CCSD(T) ), and (CCSD – CCSD(T)) for methyl iodide atmospheric reactions.

reaction	$\Delta E$ (MP2.5-CCSD(T)) (kJ/mol)	$\Delta E$ (CCSD-CCSD(T)) (kJ/mol)
[I]	1.6	-5.4
[II]	-0.9	-4
[III]	0.4	-2.9
[IV]	-7.6	-3.2
[V]	34.6	-7.8
[VI]	-1.6	6.5
[VII]	4.1	9

**Tab. 4.** The difference of the energy between (MP2.5 - CCSD(T) ), ( CCSD – CCSD(T) ) for di-iodomethane atmospheric reactions

reactions	$\Delta E$ (MP2.5-CC) (kJ/mol)	$\Delta E$ (CC-CC(T)) (kJ/mol)
[VIII]	2.1	-4.7
[IX]	6.6	-4.1
[X]	-0.6	0.4
[XI]	2.3	7.4
[XII]	34.6	-5.1
[XIII]	35.3	4.2
[XIV]	3.1	12.3
[XV]	-1.5	9.1
[XVI]	9.1	10.2
[XVII]	0.8	-1.3
[XVIII]	7.5	4.1



**Fig.1** Pictorial analysis of the performance of MP2.5 approximation.

## Conclusion

In this communication we have tested the performance of MP2.5 method for set of processes in atmosphere. The idea behind the MP2.5 is that the CCSD(T) method is quite expensive and computations even for medium-sized molecules can take long time.

The reactions selected for this test split into two groups, in the first the MP2.5 approximation works quite well, while in the second (containing IO molecule) the method fails. This can be attributed to multi-reference character of IO, indicated by one large excitation amplitude present in the CCSD calculation. The current set of reactions is too small for definite conclusions, we plan to extend it for other halogens (Br and Cl), which also play an important role in atmospheric chemistry and possibly in combination of C3 molecules to get statistically more reasonable set.

## Acknowledgement

We thank Slovak Grant Agencies VEGA (Grant 1/0092/14) and APVV (Project APVV-15-0105) for support. This work was performed in the frame of the international collaboration agreement between IRSN, Comenius University, Lille 1, and CNRS.

## References

- [1] Vogt R. (1999) Iodine Compounds in the Atmosphere, in *Reactive Halogen Compounds in the Atmosphere*, P. Fabian and N.O. Singh, (Eds.), Springer-Verlag: Berlin - Heidelberg, p. 113.
- [2] Louis F., Černušák I., Canneaux S., Mečiarová K., (2011) *Comput. Theoret. Chem.*, 965, p. 275.
- [3] Carpenter L.J. (2003) *Chem. Rev.* 103, p. 4953.
- [4] Frisch M.J., Trucks G.W., Schlegel H.B. et al., *Gaussian 09, Revision D.01*, Gaussian, Inc.: Wallingford CT, 2013.
- [5] Urban M., Černušák I., Kello V., Noga J., *Electron Correlation in Atoms and Molecules*. In *Methods in Computational Chemistry*, ed. S.E. Wilson. Vol. 1. 1987, New York: Plenum Press. p. 117.
- [6] Pitoňák M., Neogrady P., Černý J., Grimme S., Hobza P. (2009), *Chem. Phys. Chem.* 10, p. 282.