Supporting Information

Transformations of ferrates(IV, V, VI) in liquids: Mössbauer spectroscopy of frozen solutions.

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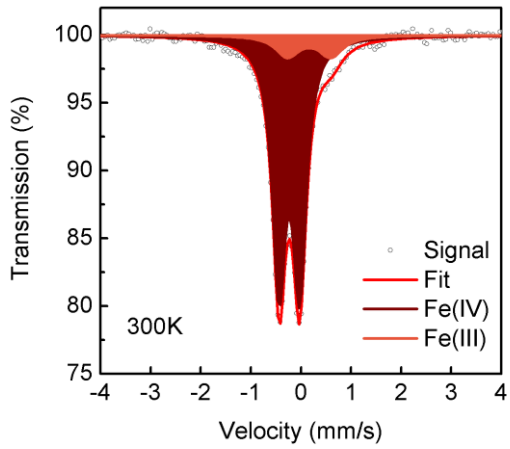

Figure SI1. ^{57}Fe Mössbauer spectrum of the starting Fe(IV) powder.

Table SI1. Hyperfine parameters and the component assignment for the ^{57}Fe Mössbauer spectrum of sodium ferrate(IV) measured at 300 K under inert atmosphere.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
Fe(IV)	Doublet	–0.23	0.41	0.32	86	Na_4FeO_4
	Doublet	0.16	0.86	0.58	14	Fe(III)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

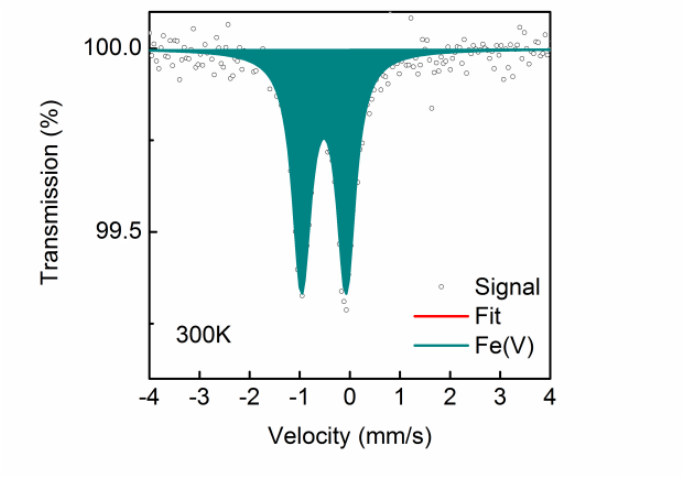

Figure SI2. ^{57}Fe Mössbauer spectrum of the starting Fe(V) powder.

Table SI2. Hyperfine parameters and the component assignment for the ^{57}Fe Mössbauer spectrum of potassium ferrate(V) measured at 300 K under inert atmosphere.

Sample	**Component**	**δ ± 0.01 (mm/s)**	**ΔE_Q ± 0.01 (mm/s)**	**Γ ± 0.01 (mm/s)**	**RA ± 1 (%)**	**Assignment**
Fe(V)	Doublet	–0.52	0.88	0.43	100	K_3FeO_4

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

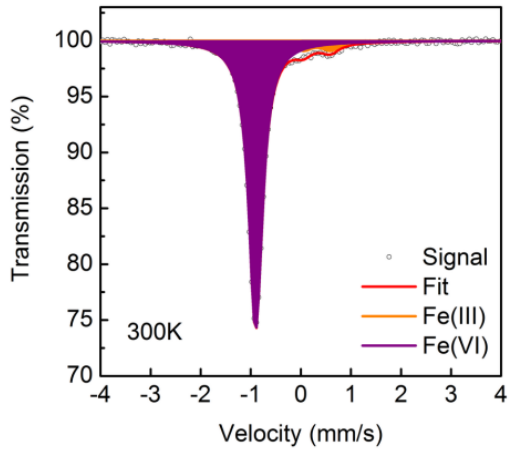

Figure SI3. ^{57}Fe Mössbauer spectrum of the starting Fe(VI) powder.

Table SI3. Hyperfine parameters and the component assignment for the ^{57}Fe Mössbauer spectrum of potassium ferrate(VI) measured at 300 K under inert atmosphere.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
Fe(VI)	Singlet	–0.90	---	0.33	92	K_2FeO_4
	Doublet	0.31	0.54	0.43	8	Fe(III)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

Table SI4. Hyperfine parameters, relative subspectral areas, and the components assignment related to low temperature (100 K) ^{57}Fe Mössbauer spectra measured on the solutions frozen after the given time interval elapsed since the contact of Fe(VI) with water molecules.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
1-2 s	Doublet	0.48	0.64	0.58	16	Fe(III)
	Singlet	–0.79	---	0.36	84	Fe(VI)
300 s	Doublet	0.48	0.65	0.52	19	Fe(III)
	Singlet	–0.79	---	0.37	81	Fe(VI)
700 s	Doublet	0.48	0.62	0.57	20	Fe(III)
	Singlet	–0.79	---	0.37	80	Fe(VI)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

Table SI5. pH values of the stirred and unstirred (marked with #) aqueous solutions containing Fe(IV), or Fe(V), or Fe(VI) in particular time intervals elapsed from the first contact of ferrate crystallites with deionized water molecules (DW).

Time (s)	pH		
	Fe(IV)+DW	Fe(V)+DW	Fe(VI)+DW
20	11.40	10.73	12.92
30	11.48	10.94	11.20
40	11.49	10.94	10.04
50	11.50	10.94	10.02
60	11.51	10.93	10.06
70	11.51	10.92	9.97
80	11.51	10.91	9.93
90	11.51	10.91	9.90
100	11.51	10.90	9.89
110	11.52	10.89	9.88
120	11.51	10.84	9.87
130	11.51	10.84	9.86
140	11.51	10.84	9.86
150	11.52	10.85	9.85
160	11.52	10.85	9.85
170	11.52	10.84	9.85
180	11.52	10.84	9.85
190	11.53	10.84	9.84
200	11.53	10.84	9.84
210	11.53	10.84	9.84
220	11.53	10.84	9.84
230	11.53	10.84	9.84
240	11.53	10.84	9.84
250	11.53	10.84	9.84
260	11.53	10.84	9.84
270	11.53	10.84	9.84
280	11.53	10.84	9.84
290	11.53	10.84	9.84
300	11.53	10.84	9.84
330	11.73#	11.07#	9.98#

Note: # pH values given for unstirred solutions of the particular composition.

Table SI6. Hyperfine parameters, relative subspectra areas, and the components assignment related to low temperature (100 K) ^{57}Fe Mössbauer spectra measured on the solutions frozen after the given time interval elapsed since the contact of Fe(V) with water molecules.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
1-2 s	Doublet	0.44	0.63	0.49	53	Fe(III)
	Singlet	-0.80	---	0.39	47	Fe(VI)
30 s	Doublet	0.44	0.61	0.52	64	Fe(III)
	Singlet	-0.80	---	0.40	36	Fe(VI)
60 s	Doublet	0.44	0.61	0.56	70	Fe(III)
	Singlet	-0.80	---	0.40	30	Fe(VI)
120 s	Doublet	0.43	0.62	0.56	84	Fe(III)
	Singlet	-0.80	---	0.37	16	Fe(VI)
230 s	Doublet	0.42	0.63	0.58	89	Fe(III)
	Singlet	-0.80	---	0.36	11	Fe(VI)
300 s	Doublet	0.43	0.62	0.57	90	Fe(III)
	Singlet	-0.80	---	0.36	10	Fe(VI)
600 s	Doublet	0.43	0.62	0.57	94	Fe(III)
	Singlet	-0.80	---	0.36	6	Fe(VI)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

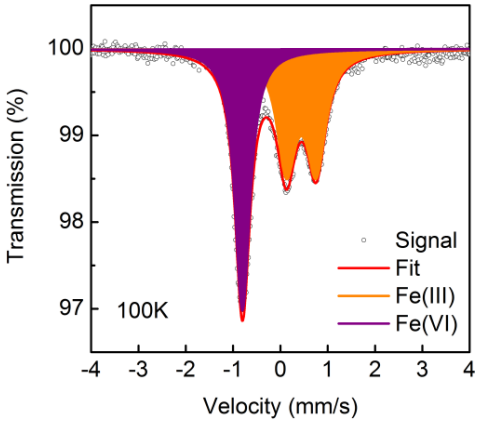

Figure SI4. ^{57}Fe Mössbauer spectrum of the solution frozen after 1-2 s of Fe(V) transformation in water.

Table SI7. Hyperfine parameters, relative subspectra areas, and the components assignment related to low temperature (100 K) ^{57}Fe Mössbauer spectra measured on the solutions frozen after the given time interval elapsed since the contact of Fe(V) with ethanol.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
1-2 s	Doublet	0.45	0.74	0.58	17	Fe(III)
	Doublet	-0.43	0.85	0.58	68	Fe(V)
	Singlet	-0.81	---	0.35	15	Fe(VI)
30 s	Doublet	0.43	0.52	0.58	43	Fe(III)
	Doublet	-048	0.69	0.36	36	Fe(V)
	Singlet	-0.81	---	0.31	21	Fe(VI)
60 s	Doublet	0.33	0.82	0.58	74	Fe(III)
	Singlet	-0.81	---	0.31	26	Fe(VI)
120 s	Doublet	0.31	0.72	0.48	74	Fe(III)
	Singlet	-0.81	---	0.32	26	Fe(VI)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

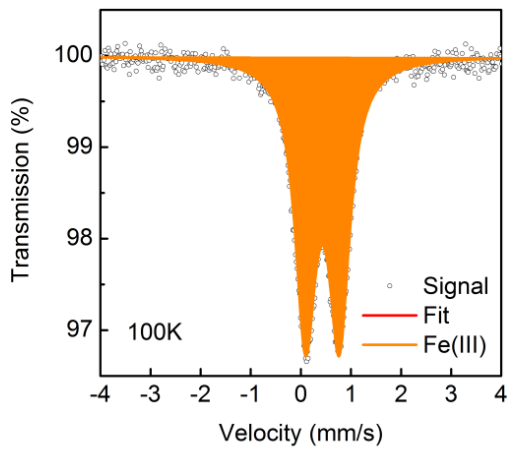

Figure SI5. ^{57}Fe Mössbauer spectrum of the solution frozen after 1-2 s of Fe(IV) transformation in H_2O.

Table SI8. Hyperfine parameters and the component assignment related to low temperature (100 K) ^{57}Fe Mössbauer spectrum measured on the solutions frozen after 1-2 s since the mixing with Fe(IV) to water.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
1-2 s	Doublet	0.43	0.68	0.50	100	Fe(III)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

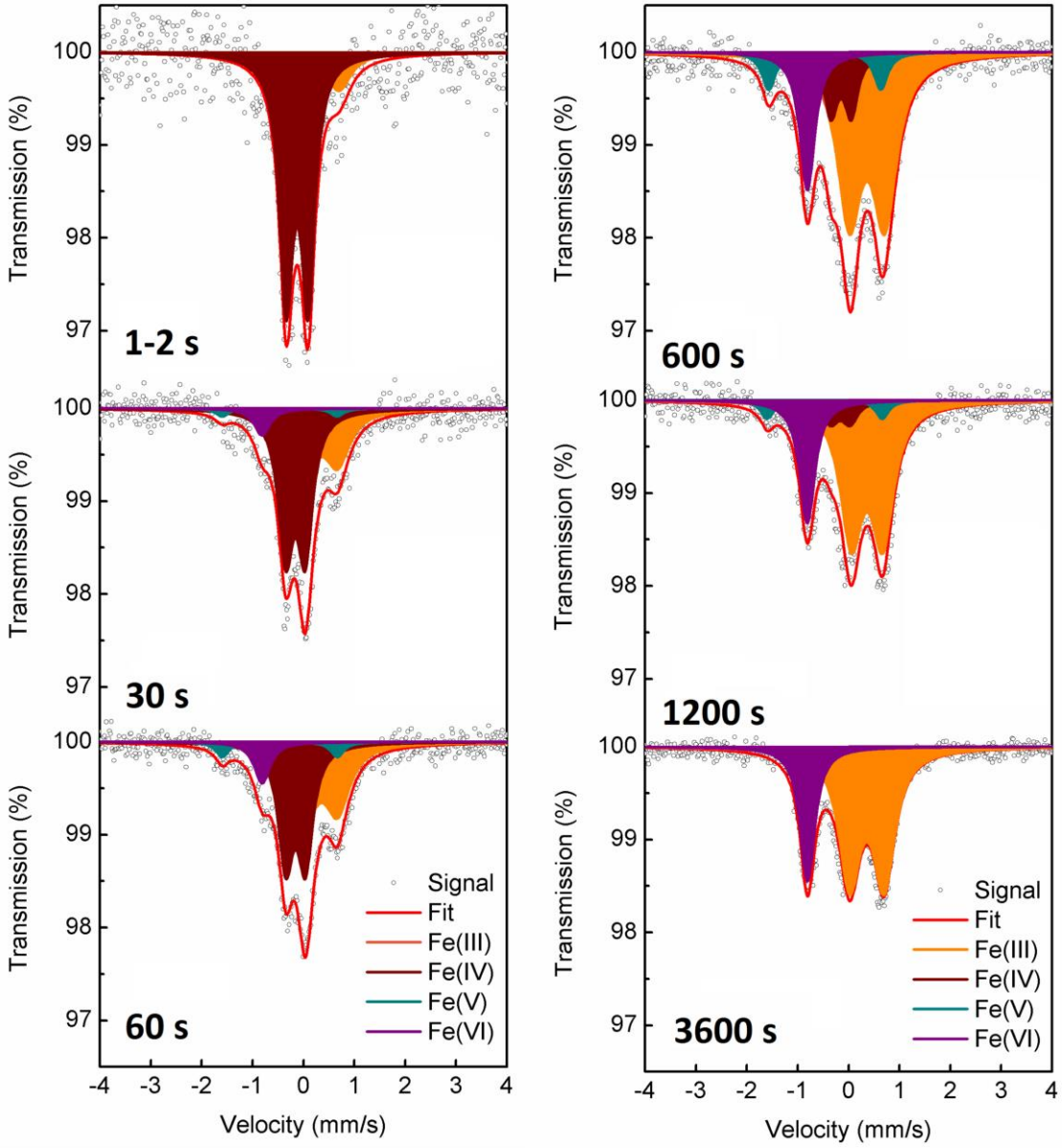

Figure SI6. ^{57}Fe Mössbauer spectra measured on the solutions frozen after the given time interval elapsed since the contact of Fe(IV) with ethanol.

Table SI9. Hyperfine parameters, relative subspectra areas, and the components assignment related to low temperature (100 K) ^{57}Fe Mössbauer spectra measured on the solutions frozen after the given time interval elapsed since the contact of Fe(IV) with ethanol.

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
1-2 s	Doublet	0.37	0.62	0.58	11	Fe(III)
	Doublet	–0.14	0.40	0.31	89	Fe(IV)
30 s	Doublet	0.37	0.62	0.58	34	Fe(III)
	Doublet	–0.15	0.38	0.36	57	Fe(IV)
	Doublet	–0.47	2.26	0.31	3	Fe(V)
	Singlet	–0.81	---	0.38	6	Fe(VI)
60 s	Doublet	0.37	0.62	0.58	41	Fe(III)
	Doublet	–0.15	0.38	0.36	45	Fe(IV)
	Doublet	–0.47	2.26	0.32	5	Fe(V)
	Singlet	–0.81	---	0.38	9	Fe(VI)
300 s	Doublet	0.37	0.63	0.58	55	Fe(III)
	Doublet	–0.15	0.38	0.36	24	Fe(IV)
	Doublet	–0.47	2.26	0.32	7	Fe(V)
	Singlet	–0.81	---	0.38	14	Fe(VI)
600 s	Doublet	0.37	0.63	0.58	62	Fe(III)
	Doublet	–0.15	0.38	0.36	13	Fe(IV)
	Doublet	–0.47	2.26	0.32	8	Fe(V)
	Singlet	–0.81	---	0.38	17	Fe(VI)
1200 s	Doublet	0.37	0.63	0.58	66	Fe(III)
	Doublet	–0.15	0.38	0.36	8	Fe(IV)
	Doublet	–0.47	2.26	0.32	5	Fe(V)
	Singlet	–0.81	---	0.38	21	Fe(VI)
3600 s	Doublet	0.37	0.63	0.58	73	Fe(III)
	Doublet	–0.81	---	0.38	27	Fe(VI)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

Table SI10. Hyperfine parameters, relative subspectra areas, and the components assignment related to low temperature (100 K) ^{57}Fe Mössbauer spectra measured on the solutions frozen after the given time interval elapsed since the contact of Fe(VI) with a mixture of ethanol-acetic acid (EtOH 140 µl + CH_3COOH 10 µl).

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	Γ ± 0.01 (mm/s)	RA ± 1 (%)	Assignment
Fe(VI)	Singlet	–0.80	---	0.38	51	Fe(VI)
	Doublet	0.47	0.73	0.53	49	Fe(III)

δ … isomer shift related to α-Fe at room temperature, ΔE_Q … quadrupole splitting, Γ … full width at half maximum, RA … relative spectral area of the individual spectral components.

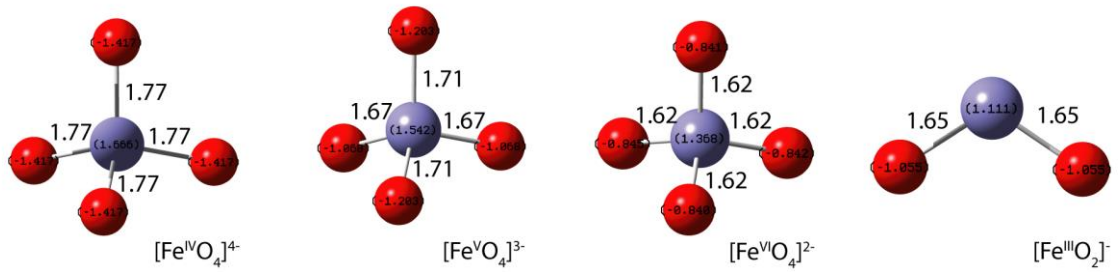

Figure SI7. Optimized structures of ferrates IV, V, VI and III in water solvent. Charges and bond lengths (in Ang) are added.

For DFT modeling we used ionic forms of equations (12)-(14) from the main text.

Two-step transformation of ferrate(IV):

$2[Fe^{IV}O_4]^{4-} + 2H_2O \rightarrow [Fe^{V}O_4]^{3-} + [Fe^{III}O_2]^{-} + 4OH^{-}$ (S1)

$[Fe^{V}O_4]^{3-} + [Fe^{IV}O_4]^{4-} + 2H_2O \rightarrow [Fe^{III}O_2]^{-} + [Fe^{VI}O_4]^{2-} + 4OH^{-}$ (S2)

The overall transformation of ferrate(IV):

$3[Fe^{IV}O_4]^{4-} + 4H_2O \rightarrow 2[Fe^{III}O_2]^{-} + [Fe^{VI}O_4]^{2-} + 8OH^{-}$ (S3)

Two-step transformation of ferrate(V):

$2[Fe^{V}O_4]^{3-} \rightarrow [Fe^{IV}O_4]^{4-} + [Fe^{VI}O_4]^{2-}$ (S4)

$[Fe^{V}O_4]^{3-} + [Fe^{IV}O_4]^{4-} + 2H_2O \rightarrow [Fe^{III}O_2]^{-} + [Fe^{VI}O_4]^{2-} + 4OH^{-}$ (S2)

The overall transformation of ferrate(V):

$3[Fe^{V}O_4]^{3-} + 2H_2O \rightarrow [Fe^{III}O_2]^{-} + 2[Fe^{VI}O_4]^{2-} + 4OH^{-}$ (S5)

Table SI11 Multiplicity *M* and spin *S* of the reactants and products of considered reactions, expectation values $\langle S^2 \rangle$, effective charges and effective electronic configurations on atoms from natural bond orbital analysis. Populations and charges are rounded-off to the first decimal place and only the important populations are reported (≥0.1). $\langle S^2 \rangle$ - $S(S+1)$ define *spin contamination,*[1] which is not significant for considered compounds.

		$[Fe^{IV}O_4]^{4-}$		$[Fe^{V}O_4]^{3-}$		$[Fe^{VI}O_4]^{2-}$		$[Fe^{III}O_2]^{-}$
$M=2S+1$		Quintet		Quartet		Triplet		Quartet
$S(S+1)$		6.0		3.75		2.0		3.75
$\langle S^2 \rangle$		6.045		3.810		2.038		3.810
Fe	1.7	$4s^{0.3}3d^{5.9}\,p^{0.1}$	1.5	$4s^{0.3}3d^{6.1}\,p^{0.1}$	1.4	$4s^{0.3}3d^{6.2}4p^{0.1}$	1.1	$4s^{0.6}3d^{6.3}$
O	-1.4	$2s^{2.0}2p^{5.5}$	-1.1	$2s^{1.9}2p^{5.2}$	-0.8	$2s^{1.9}2p^{4.9}$	-1.0	$2s^{1.9}2p^{5.1}$
O	-1.4	$2s^{2.0}2p^{5.5}$	-1.1	$2s^{1.9}2p^{5.2}$	-0.8	$2s^{1.9}2p^{4.9}$	-1.0	$2s^{1.9}2p^{5.1}$
O	-1.4	$2s^{2.0}2p^{5.5}$	-1.1	$2s^{1.9}2p^{5.2}$	-0.8	$2s^{1.9}2p^{4.9}$		
O	-1.4	$2s^{2.0}2p^{5.5}$	-1.1	$2s^{1.9}2p^{5.2}$	-0.8	$2s^{1.9}2p^{4.9}$		

References

(1) Karlický F., Otyepka M.: *Int. J. Quantum Chem.*, 114(15), 987-992, 2014.