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Photophysics of Fe(III) complexes with fluorosalicylic acid isomers in aqueous solutions



^a Institute of Chemical Kinetics and Combustion, Institutskaya 3, Novosibirsk 630090, Russian Federation

^b Novosibirsk State University, Pirogova 2, Novosibirsk 630090, Russian Federation

^c Institute of Spectroscopy, Russian Academy of Sciences, Physicheskaya 5, Troitsk, Moscow 142190, Russian Federation

^d Department of Inorganic Chemistry, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

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ABSTRACT

Transient absorption spectroscopy is used to study photophysical processes of 1:1 Fe(III) complexes with all four fluorosalicylic acid isomers (Fe-FSAs) in aqueous solutions. Excited states of Fe-FSAs decay to the ground electronic state with two time constants. The faster process is interpreted as internal conversion to the vibrationally hot electronic ground state and the slower one – as a combination of vibrational cooling and solvation of the ground state. The results obtained for Fe-FSAs and other previously investigated Fe(III) salicylato compounds allow us to reveal the main cause of photochemical stability of the complexes upon charge transfer band excitation.

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1. Introduction

Application of the results of pure chemistry often requires the ability to tune purposefully the properties of reacting species. In photochemistry one usually tunes reaction parameters in order to increase the integral quantum yield of a photochemical process [1,2] while the affected elementary processes have pico- or femtosecond timescales. In the case of complexes of transition metals it is possible to achieve fine tuning by varying the location of substituents of ligands while preserving the composition of the whole molecule. Fluorosalicylic acids exist in 4 isomeric forms and therefore represent an ideal object for the investigation of tuning of (photo)chemical properties.

We focus on iron(III) fluorosalicylato complexes due to the following reasons:

- (1) Salicylic acid, its derivatives and complexes are used for many decades as nonsteroidal anti-inflammatory, antipyretic and analgesic drugs [3–6], and therefore investigation of their chemical properties and biological activity is highly relevant.
- (2) Biological activity of organic drugs can be enhanced through incorporation of fluorine atom(s) [7–10] allowing simultaneous modulation of electronic, lipophilic and steric parameters that define pharmacodynamic and pharmacokinetic

* Corresponding author at: Institute of Chemical Kinetics and Combustion, Institutskaya 3, Novosibirsk 630090, Russian Federation.

E-mail address: pozdnyak@kinetics.nsc.ru (I.P. Pozdnyakov).

properties of drugs [9]. This observation has led to a gradual increase of occurrence of fluorine substituents in commercial pharmaceutical compounds from 2% in 1970 to more than 18% today [10].

- (3) It is desirable to determine limitations of tuning and optimization of the photochemical properties of compounds. Data on photochemical and photophysical processes will be a valuable addition to the results obtained for the same complexes in the ground state [11–13], if they are collected under comparable experimental conditions.
- (4) Fe(III) salicylato complexes are present in natural water systems and are able to modify greatly the efficiency of water treatment using Fenton and photo-Fenton processes [14,15].

Fluorosalicylic and sulfosalicylic acids have similar structure, coordination ability and absorption spectra, and their iron(III) complexes probably do not exhibit photoredox reactivity. In our previous works [16,17] devoted to aquated iron(III) 5-sulfosalicylato complexes (Fe(SSA)_n, n = 1-3) we showed that pumping the ligand-to-metal charge transfer (LMCT) band by femtosecond laser pulses results in ultrafast relaxation processes with two time constants: 0.1–0.26 ps and 1.4–1.8 ps. The faster process was interpreted as internal conversion to the vibrationally hot electronic ground state (GS) of FeSSA and the slower one – as vibrational cooling of the GS.

In the present work we investigate the photophysical properties of aqueous solutions of iron(III) complexes (Fe-FSAs) with all four fluorosalicylic acid (FSAs) isomers in order to determine the



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spectral and kinetic parameters of the excited states (ES) of the complexes, as well as to evaluate the influence of the position of fluoro substituent on deactivation parameters.

2. Experimental details

3-Fluorosalicylic acid (3-FSA, 97%, Aldrich), 4-fluorosalicylic acid (4-FSA, 96+%, Aldrich), 5-fluorosalicylic acid (5-FSA, 97%, Aldrich), 6-fluorosalicylic acid (6-FSA, 97%, Aldrich) and Fe(III) perchlorate hydrate (Aldrich) were used without further purification. The absorption spectra were recorded using Shimadzu UV 2501 PC and Agilent HP8453 spectrophotometers. Solutions were prepared using doubly distilled water.

Fe-FSAs were prepared adding Fe(III) perchlorate salt to solutions of the corresponding organic acids. The final pH of the solutions was about 2.3, concentrations of Fe(III) and FSAs were in the range of 3.4-4.8 mM. Under all conditions used in the experiments more than 90% of Fe(III) existed as the corresponding 1:1 Fe-FSA complex (see Figs. S1-S2 and Table S1 in ESI for details). Typical absorption spectra of Fe-FSAs and FSA ligands are illustrated in Fig. 1 using Fe-3FSA and 3-FSA as examples. FSA ligands exhibit an absorption band with a maximum at \sim 300 nm (π - π * transition [18]) with a moderately high molar absorption coefficient $((2.5-3.7) \times 10^3 \, \text{M}^{-1} \, \text{cm}^{-1})$. 1:1 Fe-FSAs demonstrate ligand-to-metal charge transfer (LMCT) bands with absorption maxima in the range of wavelengths from 510 to 540 nm depending on the type of organic ligand. It is worth noting that the obtained position of absorption bands and absorption coefficients are in good agreement with the corresponding values for other salicylato iron(III) complexes with similar substituents [15]. The optical properties of Fe-FSAs under study are listed in Table 1.



Fig. 1. Typical absorption spectra of FSA ligands and Fe-FSAs using 3-FSA as an example. (1) – 3-FSA, pH 2.8; (2) – Fe-3FSA complex, pH 2.3. The inset shows the structural formula of the 1:1 Fe-3FSA complex.

Table 1

Properties of 1:1 Fe(III) complexes with fluorosalicylic acid isomers.

Complex	$\lambda_{max} (nm)$	$\epsilon~(M^{-1}\times cm^{-1})$
Fe-3FSA	526	1500
Fe-4FSA	510	1400
Fe-5FSA	539	1550
Fe-6FSA	518	1500

Transient absorption spectroscopy was used to identify shortlived species in the picosecond time domain. The samples were excited by \sim 100 fs pulses at \sim 400 nm (second harmonic of a Ti: sapphire generator-amplifier system, Tsunami and Spitfire Pro XP by Spectra Physics). We used femtosecond pump-probe spectrometer ExciPro (CDP Systems) to record photoinduced absorption spectra (the details were described elsewhere [19]). The excitation energy was 5 µJ/pulse, pulse repetition rate - 1 kHz and 300 pulses were used to record a single photoinduced spectrum. The investigated solutions (total volume of 20 ml) were pumped through a 1 mm cuvette at room temperature to provide uniform irradiation and to avoid possible degradation due to photochemical reactions. The experimental data were globally fitted by a three-exponential model. The fitting program performed corrections of the group velocity dispersion and calculated the response time of the instrument.

3. Results and discussion

3.1. Ultrafast processes in Fe-FSAs

All Fe-FSAs exhibit LMCT bands, whose maxima lie in the visible region and depend on the substitution position of the fluorine atom (Table 1). The excitation of the Fe-FSAs by a femtosecond laser pulse (λ_{pump} = 400 nm) leads to the formation of a transient absorption (TA) signal, the evolution of which is presented in Fig. 2a for the Fe-3FSA complex. Immediately after excitation a bleaching was observed in the range of 440-590 nm due to the GS depopulation. The amplitude of bleaching at 526 nm corresponds to about 2.4×10^{-5} M of Fe-3FSA excited by each laser pulse (the total concentration of the complex is 4.7×10^{-3} M). The bleaching overlaps with a TA signal in the range of 600-800 nm, the latter being the manifestation of the ES population. This absorption exhibits a linear dependence on the excitation energy (Fig. 3, squares). The GS absorption of the Fe-FSAs is completely recovered after about 10 ps, that is in good agreement with the dynamics observed for related $Fe(SSA)_n$ complexes [17]. The long-lived (~300 ps) weak TA with a maximum around 700 nm that exhibits a clear quadratic dependence on the excitation energy (Fig. 3, circles) belongs to the hydrated electron [20,21] generated by the two-photon ionization of the solvent [22,23]. The generation of hydrated electron was also proved by measuring photoinduced dynamics of the pure solvent under the same conditions (data not shown).

In order to unveil the mechanism of ultrafast processes, TA decay curves of all Fe-FSAs were fitted globally by the multiexponential function (1):

$$\Delta A(\lambda, t) = \sum_{i} A_{i}(\lambda) \exp(-t/\tau_{i})$$
(1)

where $A_i(\lambda)$ and τ_i are wavelength-depended amplitudes and lifetimes respectively; $i_{max} = 2$, 3, 4. It was found that the twoexponential model provides an inappropriate fit of the experimental kinetic curves and should be ruled out. Both three- and fourexponential models provide a very good fit of almost identical quality (see Fig. S3 for details). But the results of fitting using the latter model contain an exponent with an almost zero amplitude that is



Fig. 2. Results of the ultrafast kinetic spectroscopy experiments with the Fe-3FSA complex $(4.7 \times 10^{-3} \text{ M}, \text{ pH} = 2.3)$. (a) Evolution of TA spectrum at different delay times between pump and probe pulses. (b) Kinetic curves of TA change at characteristic wavelengths. Solid lines: the best three-exponential global fit with parameters listed in Table 2.

not physically relevant. So we conclude that the three-exponential model adequately describes the observed ultrafast dynamics. For the Fe-3FSA complex the curves at several selected wavelengths and their best three-exponent global fit are presented in Fig. 2b. Delay time points from -300 fs to +300 fs were discarded because the signal in this time window is affected by the so called coherent artifact caused by nonlinear interactions between pump and probe pulses [24]. Similar results were obtained for other Fe-FSAs.

The A_1 and A_2 amplitudes in Eq. (1) describe ultrafast dynamics in Fe-FSAs complexes and the A_3 amplitude represents the hydrated electron absorption. By analogy with our previous results obtained for Fe(SSA)_n complexes [17], we propose the sequential decay of TA ($A \rightarrow B \rightarrow$ ground state) as the origin of the observed ultrafast dynamics of Fe-FSAs. In this case species-associated difference spectra (SADS) of the individual components (namely $S_A(\lambda)$ and $S_B(\lambda)$) can be calculated using Eqs. (2) and (3) derived in [25]:

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) \tag{2}$$

$$S_B(\lambda) = A_2(\lambda) \frac{\tau_2 - \tau_1}{\tau_2} \tag{3}$$

 $S_A(\lambda)$ and $S_B(\lambda)$ components that correspond to the calculated lifetimes τ_1 and τ_2 are shown in Fig. 4a together with the absorption spectrum of hydrated electron (A₃) and the inverted absorption spectrum of the Fe-3FSA complex. SADS allow one to construct optical spectra at different delay times (Fig. 4b) corresponding to different ES of the Fe-FSAs. $S_A(\lambda)$ corrected for GS



Fig. 3. The dependence of TA amplitude at 720 nm on the pump pulse energy. Squares and circles correspond to delays of 0.5 (attributed to TA of Fe-3FSA excited states) and 100 ps (attributed to hydrated electron absorption) between pump and probe pulses, respectively. Solid curves are the best linear (1) and quadratic (2) fits of these data.

depopulation is the spectrum at zero delay time, $S_B(\lambda)$ corrected for GS depopulation is the spectrum at the end of the first fast process ($\tau_1 = 0.8$ ps in the case of the Fe-3FSA complex). Immediately after excitation (zero delay time) the transient absorption spectrum contains a wide band with a maximum at ~670 nm (Fig. 4b, curve 1). This band is assigned to the Frank-Condon excited state (F.C.-ES) of the complex. The absorption spectrum of this state exhibits a significant red shift (~140 nm) relative to the GS absorption spectra (Fig. 4b, curves 1 and 3, Table 2). This fact indicates the existence of higher-lying exited states of the Fe-FSAs. After the first fast process (τ_1) is finished, the absorption band is blue-shifted and has a maximum at $\lambda \sim 580$ nm (Fig. 4b, curve 2). Similar results were obtained in pump-probe experiments with aqueous solutions of other Fe-FSAs (Table 2).

3.2. Mechanism of ES relaxation of the Fe-FSAs

Several main processes can occur in the (sub)picosecond time scale upon excitation of the charge transfer (CT) band of transition metal complexes [26,27]:

- 1. Electronic transition(s) between different ESs (including population of the initial GS).
- 2. Vibrational cooling of GS or ES that manifests itself as a narrowing of the observed TA band.
- 3. Solvent relaxation that leads to a blue shift of the observed TA band.

Another important feature of the photophysics of coordination compounds is the possible coincidence of characteristic times of physically different processes that appear as a single process in measured decay traces [27]. In the case of Fe-FSAs a biphasic



Fig. 4. Results of the ultrafast kinetic spectroscopy experiments with the Fe-3FSA complex $(4.7 \times 10^{-3} \text{ M}, \text{pH} = 2.3)$. (a) Species associated difference spectra (SADS) obtained from the three-exponential global fit (Eq. (1)) of kinetic curves. (1) – Spectrum at zero delay time, $S_A(\lambda)$; (2) – spectrum after the end of the ultrafast process, $S_B(\lambda)$; (3) – absorption spectrum of hydrated electron (A₃); (4) – inverted absorption spectrum of the Fe-3FSA complex. (b) 1 – spectrum of the F.-C. ES ($S_A(\lambda)$ corrected for GS depopulation); 2 – spectrum of the unrelaxed GS ($S_B(\lambda)$ corrected for GS depopulation). The solid curve (3) represents the GS absorption spectrum of the Fe-3FSA complex ($2.4 \times 10^{-5} \text{ M}$). The Jablonski diagram in the inset demonstrates the photophysics of Fe-FSAs.

Table 2

Lifetimes and absorption maxima of excited states of Fe(III) complexes with fluorosalicylic acid isomers obtained from the global three-exponential fit of the experimental data.

Complex	τ_1 (ps)	$\lambda_{max}\left(\tau_{1}\right)\left(nm\right)$	τ_2 (ps)	$\lambda_{max}\left(\tau_{2}\right)\left(nm\right)$
Fe-3FSA	0.8 ± 0.1	670	2.6 ± 0.3	580
Fe-4FSA	0.5 ± 0.1	660	2.0 ± 0.2	580
Fe-5FSA	0.6 ± 0.1	695	2.1 ± 0.2	610
Fe-6FSA	0.9 ± 0.1	645	2.8 ± 0.4	555
Fe-4FSA Fe-5FSA Fe-6FSA	0.5 ± 0.1 0.6 ± 0.1 0.9 ± 0.1	660 695 645	2.0 ± 0.2 2.1 ± 0.2 2.8 ± 0.4	580 610 555

dynamics with characteristic lifetimes of 0.5–0.9 ps and 2.0–2.8 ps was observed (Table 2). To explain this dynamics both the kinetic and spectral data should be taken into account. After the end of the first process a pronounced blue shift of transient absorption spectra by 80–90 nm relative to the absorption spectrum of the F.-C. ES was observed (Fig. 4b, curves 1 and 2, Table 2). This shift is too large to be explained by vibrational cooling or solvation of the F.-C. ES. The fast (<10 ps) recovery of the GS absorption of Fe-FSAs allows us also to exclude population of a lower-lying ES that is usually rather long-lived and decays into a GS on the (sub)-nanosecond time scale [27–29]. We assume that the first process is an ultrafast back electron transfer (ET) to the vibrationally hot electronic GS. Indeed, the characteristic time of several hundreds of femtoseconds is typical for electronic transitions in transition

metal complexes [26,27]. Moreover, this explanation is in agreement with our previous results obtained in experiments with iron(III) complexes with sulfosalicylic acid [17]. It is worth noting that the absorption maximum of the hot GS of Fe-FSAs is also red-shifted relative to the maximum of the thermalized GS and the width of the former is larger. These facts can be explained by an incomplete solvent relaxation (characteristic times of diffusional solvation in water are about 1–2 ps [30,31]) and by redistribution of vibrational energy of the hot GS among several vibrational modes.

Thus, the second time constant τ_2 is attributed to both vibrational cooling and solvation of the GS. The situation when different processes have similar characteristic times and manifest themselves as a single process is frequent in photophysics of coordination compounds [27]. It is worth noting that characteristic values of τ_2 are the same within the limits of experimental error (mean value $\approx 2.4 \text{ ps}$) for all Fe-FSAs and coincide with the corresponding times of vibrational cooling obtained for complexes in aqueous solutions by other scientific groups [32–34] and also with the values for Fe(SSA)_n complexes [17]. The only difference between ultrafast dynamics of Fe(SSA)_n and Fe-FSAs is the shorter time of back ET in the case of the former species (about 0.2 ps). In order to explain this fact one needs additional information on the influence of different substituents in the benzene ring of salicylic acid derivatives on the GS recovery process.

4. Conclusion

The femtosecond pump-probe technique was applied to investigate photophysical properties of aqueous solutions of Fe(III) complexes with fluorosalicylic acid isomers. The biphasic dynamics of GS recovery upon excitation of LMCT bands of Fe-FSAs was observed. The shorter time constant ($\tau_1 = 0.5-0.9 \text{ ps}$) is ascribed to back ET to the vibrationally hot electronic GS of Fe-FSAs and the second time constant (τ_2 = 2.1–2.8 ps) is assigned to vibrational cooling and solvation of the GS. Obtained results on the photophysics of $Fe(SSA)_n$ [17] and Fe-FSAs together with the data on the photochemistry of other Fe(III) salicylato compounds [15,16] allowed us to conclude that an ultrafast back ET in the Frank-Condon excited state is the main cause of the observed photochemical stability of complexes exposed to the laser light at wavelengths inside the LMCT band. This fact is important because Fe(III) salicylato complexes are present in natural water systems and can influence greatly the efficiency of water treatment using Fenton and photo-Fenton processes [14,15].

In order to establish connection between the position of the fluorine atom in fluorosalicylic acids and their ground-state and excited-state properties a knowledge of quantitative parameters related to fluorine atoms, hydroxyl and carboxylate groups is necessary. To date no information on XPS spectra, Hammett constants or other parameters related to the fluorine atom position are available except the ¹⁹F NMR spectra. In order to arrive at conclusions that will allow purposeful modification of properties of complexes further experimental data are needed. Making a step in this direction we have shown in the present study that the spectra and ultrafast dynamic of GS recovery in Fe-FSAs are influenced by the fluorine atom position, but this influence is rather small.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2016.08. 028.

References

- [1] J. Šima, Optimizing the photoreactivity of chemical compounds necessity, challenges and obstacles, in: T.W. Cartere, K.S. Verley (Eds.), Coordination Chemistry Research Progress, Nova Science Publishers, New York, 2008, pp. 71–102.
- [2] J. Šima, Photochemical reactions of iron(III) complexes classification, mechanisms, and application, in: A. Sánchez, S.J. Gutierrez (Eds.), Photochemistry Research Progress IB, Nova Science Publishers, New York, 2008, pp. 103–160.
- [3] J.E. Weder, C.T. Dillon, T.W. Hambley, B.J. Kennedy, P.A. Lay, J.R. Biffin, H.L. Regtop, N.M. Davies, Copper complexes of nonsteroidal anti-inflammatory drugs: an opportunity yet to be realized, Coord. Chem. Rev. 232 (2002) 95–126.
- [4] R.K. Madan, J. Levitt, A review of toxicity from topical salicylic acid preparations, J. Am. Acad. Dermatol. 70 (April) (2014) 788-792.
- [5] A.S. Hawley, M.D. Fullerton, F.A. Ross, J.D. Schertzer, C. Chevtzoff, K.J. Walker, M.W. Peggie, D. Zibrova, K.A. Green, K.J. Mustard, B.E. Kemp, K. Sakamoto, G.R. Steinberg, D.G. Hardie, The ancient drug salicylate directly activates AMPactivated protein kinase, Science 336 (May) (2012) 918–922.
- [6] A. Lawal, J.A. Obaleye, Synthesis, characterization and antibacterial activity of aspirin and paracetamol-metal complexes, Biokemistri 19 (2007) 9–15.
- [7] Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J.L. Aceña, V.A. Soloshonok, K. Izawa, H. Liu, Next generation of fluorine-containing pharmaceuticals, compounds currently in phase II-III clinical trials of major pharmaceutical companies: new structural trends and therapeutic areas, Chem. Rev. 116 (2016) 422–518.
- [8] M. Cametti, B. Crousse, P. Metrangolo, R. Milani, G. Resnati, The fluorous effect in biomolecular applications, Chem. Soc. Rev. 41 (2012) 31–42.
- [9] F.M.D. Ismail, Important fluorinated drugs in experimental and clinical use, J. Fluorine Chem. 118 (2002) 27–33.
- [10] Ch. Isanbor, D. O'Hagan, Fluorine in medicinal chemistry: a review of anticancer agents, J. Fluorine Chem. 127 (2006) 303–319.
- [11] T. Szabó-Plánka, B. Gyurcsik, I. Pálinkó, N.V. Nagy, A. Rockenbauer, R. Šípoš, J. Šima, M. Melník, Effect of fluorine position on the coordinating ability of fluorosalicylic acids an experimental study complemented with computations, J. Inorg. Biochem. 105 (2011) 75–83.
 [12] J. Šima, M. Izakovič, R. Šipoš, J. Švorec, Effect of fluoro-containing ligand and/or
- [12] J. Šima, M. Izakovič, R. Šípoš, J. Švorec, Effect of fluoro-containing ligand and/or fluoride on photoredox stability of iron(III) complexes, Acta Chim. Slov. 54 (2007) 268–272.
- [13] R. Šípoš, J. Šima, B. Gyurcsik, Solution properties of iron(III) complexes with 4fluorosalicylic acid – spectra and speciation, Chem. Listy 106 (2012) 509.
- [14] D.A. Nichela, A. Donadelli, B. Caram, M. Haddou, F. Rodriguez Nieto, E. Oliveros, F.S. Garcia Einschlag, Iron cycling during the autocatalytic decomposition of benzoic acid derivatives by Fenton-like and photo-Fenton techniques, Appl. Catal. B Environ. 170 (2015) 312–321.
- [15] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, E. Oliveros, Photochemistry of Fe(III) complexes with salicylic acid derivatives in aqueous solutions, J. Photochem. Photobiol. A: Chem. 307 (2015) 9–15.

- [16] I.P. Pozdnyakov, V.F. Plyusnin, V.P. Grivin, D.Yu. Vorobyev, N.M. Bazhin, S. Pages, E. Vauthey, Photochemistry of Fe(III) and sulfosalicylic acid aqueous solutions, J. Photochem. Photobiol. A: Chem. 182 (2006) 75–81.
- [17] I.P. Pozdnyakov, V.F. Plyusnin, N. Tkachenko, H. Lemmetyinen, Photophysics of Fe(III) – sulfosalicylic acid complexes in aqueous solutions, Chem. Phys. Lett. 445 (2007) 203–207.
- [18] A.L. Sobolewski, W. Domcke, Ab initio study of excited-state intramolecular proton dislocation in salicylic acid, Chem. Phys. 232 (1998) 257–265.
- [19] S.V. Chekalin, The unique femtosecond spectroscopic complex as an instrument for ultrafast spectroscopy, femtochemistry and nanooptics, Phys. Usp. 49 (2006) 634–641.
- [20] P.M. Hare, E.A. Price, D.M. Bartels, Hydrated electron extinction coefficient revisited, J. Phys. Chem. A 112 (2008) 6800–6802.
- [21] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ('OH/O') in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513.
- [22] J.L. McGowen, H.M. Ajo, J.Z. Zhang, B.J. Schwartz, Femtosecond studies of hydrated electron recombination following multiphoton ionization at 390 nm, Chem. Phys. Lett. 231 (1994) 504–510.
- [23] Y. Kimura, J.C. Alfano, P.K. Walhout, P.F. Barbara, Ultrafast transient absorption spectroscopy of the solvated electron in water, J. Phys. Chem. 98 (1994) 3450– 3458.
- [24] L. Palfrey, T.F. Heinz, Coherent interactions in pump-probe absorption measurements: the effect of phase gratings, J. Opt. Soc. Am. B 2 (1985) 674– 679.
- [25] A.S. Rury, R.J. Sension, Broadband ultrafast transient absorption of iron(III) tetraphenylporphyrin chloride in the condensed phase, Chem. Phys. 422 (2013) 220–228.
- [26] L.S. Forster, Intersystem crossing in transition metal complexes, Coord. Chem. Rev. 250 (2006) 2023–2033.
- [27] A. Vlcek Jr., The life and times of excited states of organometallic and coordination compounds, Coord. Chem. Rev. 200–202 (2000) 933–978.
- [28] A.C. Bhasikuttan, M. Suzuki, S. Nakashima, T. Okada, Ultrafast fluorescence detection in tris(2,2'-bipyridine)ruthenium(II) complex in solution: relaxation dynamics involving higher excited states, J. Am. Chem. Soc. 124 (2002) 8398– 8405.
- [29] J.E. Monat, J.K. McCusker, Femtosecond excited-state dynamics of an iron(II) polypyridyl solar cell sensitizer model, J. Am. Chem. Soc. 122 (2000) 4092– 4097.
- [30] P.J. Reid, C. Silva, P.F. Barbara, L. Karki, J.T. Hupp, Electronic coherence, vibrational coherence, and solvent degrees of freedom in the femtosecond spectroscopy of mixed-valence metal dimers in H₂O and D₂O, J. Phys. Chem. 99 (1995) 2609–2616.
- [31] A. Thaller, R. Laenen, A. Laubereau, Femtosecond spectroscopy of the hydrated electron: novel features in the infrared, Chem. Phys. Lett. 398 (2004) 459–465.
- [32] D.H. Son, P. Kambhampati, T.W. Kee, P.F. Barbara, Femtosecond multicolor pump-probe study of ultrafast electron transfer of [(NH₃)₅Ru^{III}NCRu^{II}(CN)₅]⁻ in aqueous solution, J. Phys. Chem. A 106 (2002) 4591–4597.
 [33] K. Tominaga, D.V. Kliner, A.E. Johnson, N.E. Levinger, Femtosecond
- [33] K. Tominaga, D.V. Kliner, A.E. Johnson, N.E. Levinger, Femtosecond experiments and absolute rate calculations on intervalence electron transfer of mixed-valence compounds, J. Chem. Phys. 98 (1993) 1228–1243.
- [34] A.V. Tivanski, C. Wang, G.C. Walker, Vibrational mode coupling to ultrafast electron transfer in [(CN)₅OsCNRu(NH₃)₅]⁻ studied by femtosecond infrared spectroscopy, J. Phys. Chem. A 107 (2003) 9051–9058.