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XAFS IN THE TRACKING OF REACTIONS IN AQUEOUS SOLUTION: A CASE OF REDOX REACTION BETWEEN [AuCl$_4$]$^-$ COMPLEX IONS AND ETHANOL

METODA XAFS W BADANIACH REAKCJI ZACHODZĄCYCH W ROZTWORACH WODNYCH: PRZYKŁAD REAKCJI REDOKS POMIĘDZY JONAMI KOMPLEKSOWYMI [AuCl$_4$]$^-$ I ALKOHOLEM ETYLOWYM

In this work the potential application of synchrotron radiation in the studies of reaction kinetics in aqueous phase were presented. After short introduction describing principles of technique and potential application of XAFS for the structural studies of reacting species, the experimental results of kinetic measurements of reaction between gold(III) chloride complex ions and ethanol were presented. Analyzing the changes of absorption intensity in the XANES spectra registered at Au-L_3 edge during the reaction, the change of the valence state of Au central atom (form 3+to 0) of reacting complex ion was determined. Moreover, empirical XANES data gave the chance to register the kinetic curve and to determine the rate constant of the studied reaction. It was found that reaction is relatively slow (second-order rate constant $k = 3.66 \cdot 10^{-5}$ M^{-1}s) and lead to the gold metallic phase formation in the system. Applying the continuous-flow method, within the first 600 ms of reaction the changes in XANES spectra were registered. From the obtained results, supported with numerical calculations, two intermediate forms of adducts appearing prior the electron transfer were suggested. It was concluded that when the classic methods, e.g. UV-Vis spectrophotometry, cannot be applied to studies of kinetics of reactions in aqueous solution, the XAFS technique can be a valuable and substitutive (or supplementary) tool for such measurements.

Keywords: XAFS, XANES, redox reaction, gold complex ions, ethanol

W pracy przedstawiono potencjalne możliwości zastosowania promieniowania synchrotronowego w badaniach nad kinetyką reakcji przebiegających w roztworach wodnych. We wstępie, omówiono podstawy techniki rentgenowskiej analizy struktury nadsubtelnej (XAFS) i jej możliwości zastosowania w badaniach strukturalnych związków chemicznych w fazie ciekłej. Zaprezentowano również dane eksperymentalne z pomiarów XAFS dotyczące kinetyki reakcji pomiędzy chlorkowymi kompleksami złota(III) i alkoholem etylowym. Z analizy zmian intensywności absorpcji widm XANES rejestrowanych przy krawędzi L_3 złota określono zmianę stopnia utlenienia atomu centralnego Au (z 3+ do 0) reagującego kompleksu. Ponadto, dane empiryczne pozwoliły na wyznaczenie krzywej kinetycznej oraz określenie drugorzędowej wartości stałej szybkości reakcji (k = 3.66 · 10^{-5} M^{-1}s). W wyniku analizy widm XANES potwierdzono powstawanie faza metalicznej złota w układzie. Stosując metodę ciągłego przepływu reagentów, zarejestrowano zmiany w widmie XANES w ciągu 600 ms od rozpoczęcia reakcji. Na podstawie zarejestrowanych widm oraz przeprowadzonych obliczeń numerycznych zasugerowano dwie możliwe struktury adduktu tworzącego się przed właściwym transferem elektronu w reakcji redoks. Z przeprowadzonych eksperymentów wynika, że w układach, w których nie jest możliwe stosowanie spektrofotometrii UV-Vis, metoda XAFS może być zastępczym i obiecującym narzędziem do badan kinetyki reakcji.

1. Introduction

Experimental techniques used in the studies of reaction kinetics invariably lead to the determination of the rate constants of the reaction as well as to the identification of variables, that affect the rate of reaction. Usually, to establish the rate law, a time evolution dependence of the reactants (or products) concentration and some-times also the catalyst is determined. This can be done in a direct or an indirect way, depending on the relation existing between the concentration and the physical property to be measured. Except for direct concentration measurements (e.g. sampling) other physical properties, such as pressure, electrical conductivity, electrode potential, density, refractive index and absorbance, can

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be probed. The typical assumption is, that the property varies linearly with the concentration. Moreover, many factors, especially temperature and experiment timing, must be controlled with special attention, since their deviation may significantly affect the results of experiments. These problems were discussed and explained in a number of excellent books dealing with chemical kinetics, for instance ref. [1-4].

However, reactions almost never go as written. Usually, "the path" from the substrates to products goes through the number of subsequent steps. Fortunately, on one hand, development of experimental methods shortened the time scale of experimental detection and made possible observation of these changes. On the other hand, enormous theoretical progress has been made to understand the mechanism of the reaction. The *transition state theory* (TST) put forward by Henry Eyring [5] and Evans and Polanyi [6] appeared to be very fruitful and resulted in a number of theoretical speculations, but the existence of so-called activated complex was difficult to check experimentally [7]. For an elementary reaction during product formation the change in intermolecular distance is of the order of 10 Å. Assuming that the encounter atoms move with the speed between 10^4 and 10^5 cm/s, to cover this distance it takes about 10^{-12} to 10^{-11} s. Thus, time available for observation of such a process must be of the picoseconds in order of magnitude. Moreover, to achieve good resolution of measurement, this time must go further down to the femtosecond scale. It was Ahmed Zewail [8] who combining molecular-beam and pulsed-laser techniques managed to reduce observation time to the femtoseconds scale. However, to interpret the data one must be able to calculate the spectra of the activated complex in its transition state for a number of different structures. This simply cannot be done without computer modeling, and consequently it became an inseparable part of the data processing. As for the future, there is still a hope that, as laser technologies develop further, a creation of shorter pulses can be expected leading to the experimental technique probing chemical transformations in attoseconds.

Among the different experimental method, e.g. UV-Vis spectrophotometry [9] or Dynamic Light Scattering (DLS) [10] which can be helpful in determination of kinetics reaction and suggestion of reaction mechanism is X-ray Absorption Fine Structure (XAFS) spectroscopy. It is highly versatile technique i.e. it can be applied to the solids, liquids as well as gaseous states. In recent years, this new powerful and sophisticated, analytical method was significantly improved. At synchrotron facility, high intensity radiation source provides X-ray beam of finely tunable energy, which is used to study materials at the atomic level. Good introduction to this particular technique was recently given by Bunker [11]. The possibility of the application of this technique to the chemical systems was discussed already 30 years ago by Teo [12]. It is commonly used in the studies of heterogeneous reactions. It can also be used for the studies in aqueous solutions (is a very promising tool to studies in the systems in which other techniques, like e.g. spectrophotometry, cannot be applied), especially to:

– *in situ* studies of structural changes in the system at atomic level,
– register of progress of oxidation/reduction reactions and detection of structural changes connected with the electron transfer process,
– detect of changes in the valence state of metal ions, etc.

XAFS provides information on the valence state of an absorbing atom, and combined with electrochemical technique has been used e.g. in spectroelectrochemistry [13] providing the means to study changes in the bond length and coordination number of atom neighbours to the absorber. It has been also employed in the characterization of a number of catalysts used in low temperature fuel cells [14], in particular carbon supported Pt electrocatalysts. An interesting approach to the study of chemical reactions was suggested by Ohtaki [15]. He suggested that using XAS the structure of reactions intermediates can be determine, which help to explain the mechanism of complex reactions in solutions. He proposed a measurement scheme based on combination of XAFS with stopped-flow technique (SF). In the subsequent papers [16, 17] Ohtaki and coworkers showed that it is possible to construct SF-XAFS apparatus and to determine the structure of the reaction intermediates formed during the dynamic processes. Recently XAFS was applied for instance to study the mechanism of Pt clusters formation within AOT reversed micelles [18] or to initial step of nucleation of Au clusters via reduction of $[AuCl_4]^-$ complex ions in aqueous solutions [19]. Thus, the power of XAFS can also be very useful in studying redox reactions in aqueous solutions, which lead to the formation of metallic nanoparticles.

In this paper we present XAFS principles that are important in the study of aqueous solutions followed by discussion of the difficulties and outcomes of the measurements of the redox reaction between gold(III) complex ions and ethanol.

2. Principles

Synchrotron radiation appears when the path of electrons, running almost at the speed of light, is curved by external magnetic field. Electrons moving along curved path in the synchrotron ring accelerate and generate

strong electromagnetic radiation of a wide spectrum from infrared to γ-rays. At first, in the years 40-60's of XX century, synchrotron radiation was considered as a spurious "by-product" at synchrotron facility built for high-energy physics experiments. Now, after four decades of rapid development, it is a routinely used source of intense, coherent, and time patterned source of tunable electromagnetic radiation, especially unique in the X-ray range. The radiation generated by curved electron beam exits to beamlines situated around the storage ring, and each end-station is dedicated to different type of experiments. The cartoon scheme of synchrotron facility including main elements of the X-ray optics used for XAFS experiments is shown in Fig. 1 *a*, while pictures *b* and *c* presents examples of the setups used for studying reactions in the solutions.
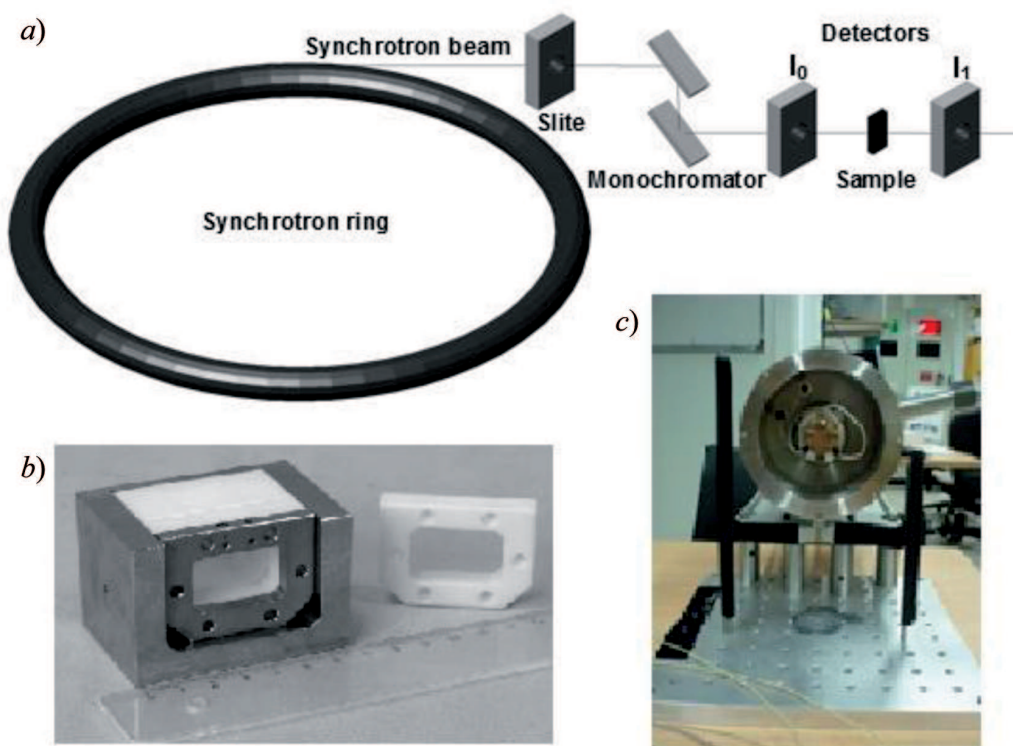

Fig. 1. *a*) Sketch of XAFS beamline including main elements of the X-ray optics and detection system. Examples of the cell compartment applied in the XAFS measurements reported in this paper: *b*) – from Hasylab/DESY in Hamburg, Germany, *c*) – from ESRF in Grenoble, France
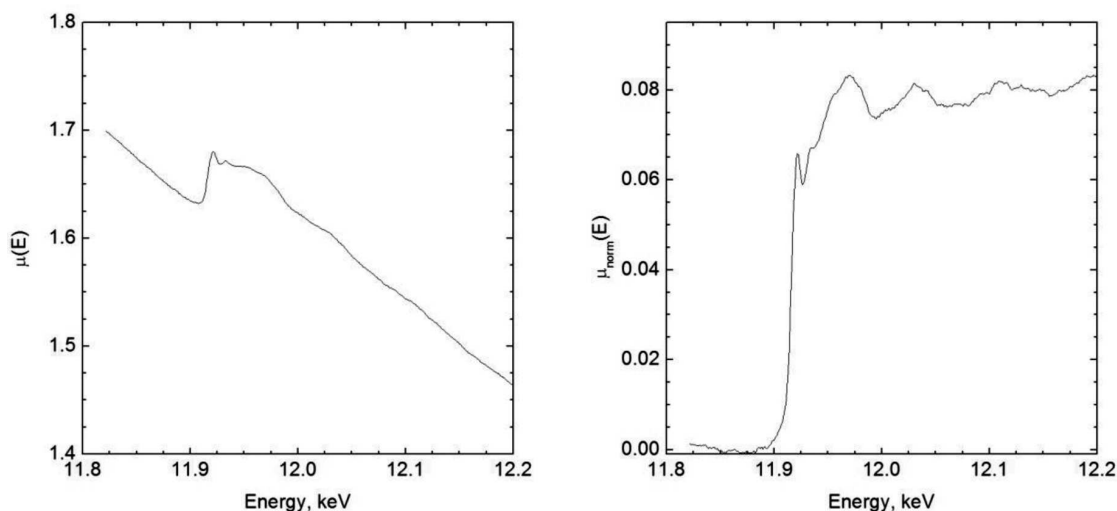

Fig. 2. Dependence of gold absorption coefficient (μ) vs. energy (E) in the vicinity of Au L_3 absorption edge: *a*) as measured, *b*) after pre-edge subtraction. Conditions: aqueous solution of gold(III) chloride complex ions, $C_{0,Au(III)} = 1 \cdot 10^{-3}$ M, pH =1, ambient temperature ($\approx 22°C$)

If the XAFS experiments are carried out in transmission mode, the initial intensity of radiation (I_0) will change across the sample of the thickness x according to the Beer-Lambert law:

$$I = I_0 exp(-\mu x) \qquad (1)$$

where μ is the mass absorption coefficient, that depends on the absorbing material and it varies with the energy of incident radiation (photons). This particular dependence, namely $\mu(E)$ over the energy range in the vicinity of absorption edges, is determined during experiment. The typical $\mu(E)$ dependence is shown in Fig. 2a.

Pre-edge subtracted $\mu(E)$ dependence (Fig. 2b) is often normalized to the value above the energy edge to allow for straightforward comparison of spectral features for the samples of different concentrations of absorbing species. The near edge analysis of X-ray absorption spectra, that is typically performed in the range from -20 to 150 eV with respect to the edge energy (i.e. the first inflection point in the absorbing spectrum), provides the information about chemistry of the absorber. It is often called X-ray Absorption Near Edge Structure (XANES). The shape, the position of absorption edge and the maximum of absorption coefficient (called "white line") provide the information on local structure (coordination) and valence state of the absorbing atom. The changes in the intensity of the "white line" reflect the density of unoccupied states (5d-states in the case of Au L_2 and L_3 edges) and indicate the state of oxidation of the atom. In turn, the change in the peak's area reflects changes in local coordination of atoms. Oscillations, which are seen above the edge energy in the energy range of hundreds of eV are the subject to Extended X-ray Absorption Fine Structure (EXAFS) analysis. Absorption coefficient $\mu(E)$ contains oscillatory part $\chi(k)$, which origins in the interference of the wave functions of excited photoelectrons and photoelectrons scattered by neighboring atoms, that can be extracted from the spectra and displayed in wave-vector k-space (Fig. 3a). It provides information on the structure of local environment and interatomic distances that can be obtained upon Fourier transform (FT) of $\chi(k)$ dependence into real space (Fig. 3b). Thus, the XAFS technique, both in near edge and extended range, may be utilized to track changes in the coordination, symmetry and electron density of the reacting system.

If the reaction of gold(III) reduction in aqueous solution is investigated, XAFS experimental data enable to track the following processes.

– Since the change of the intensity of the "white line" depends on the density of unoccupied states (5d-states), it reflects the oxidation state of the metal. A decrease in intensity means the filling of these states, that is equivalent to reduction of the oxidation state. If the spectral area under the "white line" is identical with that of pure metal (the density of the unoccupied states decreases), it means that the state of metal's oxidation falls to zero. Thus, the process of aqueous complexes reduction can be followed in a straightforward way.

– Evolution in the spectral shape (the energy position and intensity of certain features) reflects the changes in the local coordination of Au ions. In the reaction process it is usually associated with the evolution of the structure of molecule, i.e. ligands are incorporated.
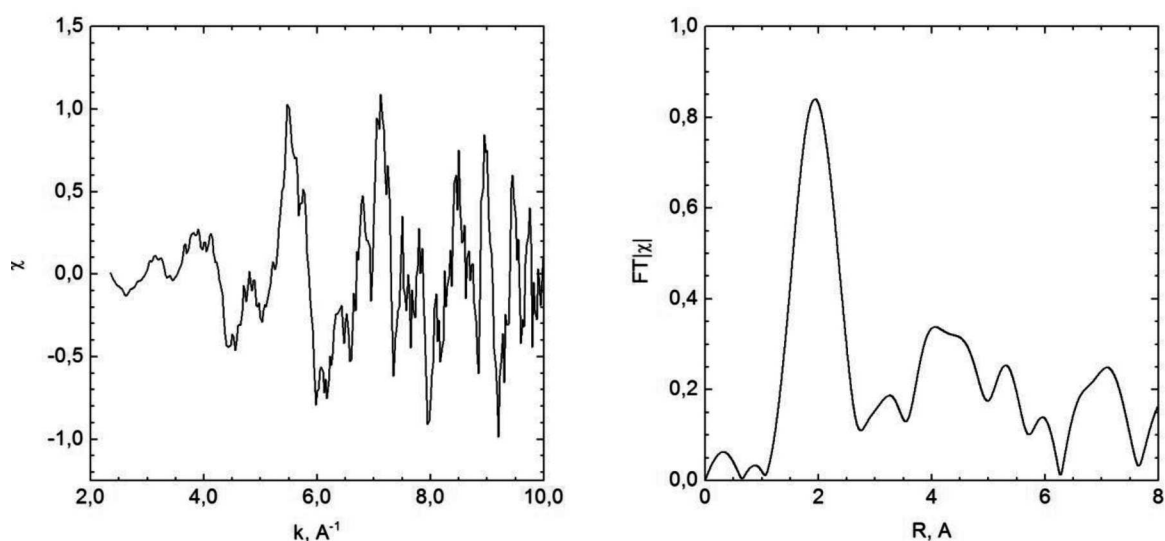

Fig. 3. EXAFS spectra of the studied systems: *a*) presented in the *k*-space – dependence of $\chi(k)$ vs. *k* wave-vector, *b*) after Fourier transformation

- The appearance of distinct features at the energy above "white line" is usually associated with hybridization of metallic states with unoccupied states of the neighbours (e.g. 3d states of Cl). If this features evolve with an increase of the reductant concentration, is likely because the exchange of ligands of Au central atom (e.g. Cl$^-$ → OH$^-$).
- Fourier Transform of EXAFS oscillations provides the information about interatomic distances. For the initial state of the solution (before reaction) the main peak gives the average distance between Au and neighbor atoms in the complex (Fig. 3b). Decrease of this peak position with reductant addition, that indicate the lowering of interatomic distances, is attributed to creation of (shorter) metal–metal bond. In this way the distance between near neighbours and the coordination number can be determined in the range of few Angstroms.

3. Experimental

3.1. Materials

HAuCl$_4$ solution was prepared by dissolving of pure gold (99.99 % purity, obtained from Mennica Państwowa, Poland) in aqua regia. After several evaporations of this solution and dilution of the obtained solid in distilled water, the starting substrate was obtained which was next used for solutions preparation with fixed gold content. These solutions were protected from the sunlight. Ethyl alcohol solution was prepared using pure grade chemical from POCh (Gliwice, Poland) and deionized water as a solvent.

3.2. Technique

The reaction between gold(III) chloride complex ions (5·10^{-3} M [AuCl$_4$]$^-$ in 0.5 M NaOH) and ethyl alcohol (96% dissolved with H$_2$O as 1:10) was carried out at ambient temperature (22.5°C) using two different cell compartments. The first reactor (Re1), working within the stopped-flow principle, was constructed at the Hasylab/DESY (Hamburg, Germany) and is shown in Fig. 1b. It was working in transmission detection mode and was already used in our previous experiments [20]. The second one (Re2), working within the continuous-flow principle, shown in Fig. 1c, was available during the experiments performed in high resolution fluorescence detection (HERFD) mode at ID26 beamline of ESRF (Grenoble, France). It was constructed in-house under the guidance of dr Tsu-Chien Weng. The continuous flow setup allowed for higher temporal resolution, of the order of milliseconds, in the detection of XAFS spectra during

the reaction. Both reactors were made of non-reactive materials in order to protect against gold cementation.

Structures of reactants were calculated and generated using HyperChem 7 software [21]. Kinetic equations were fitting using TCCurve 2.0 software [22].
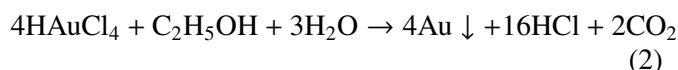
3.3. Experimental Procedure

To initiate the reaction, reactants were injected into the cell of the reactor with the volume ratio 1:1. For the Re1, injection of reactants was made using two independent syringes equipped with slim, polymeric needles. For the Re2, solutions containing were mixed using syringe pumps in tubular glass cell. Knowing geometry (diameter and length) of the tubes and the flow rate of reactants it was possible to reach different time (τ) after beginning of the reaction.

After mixing the reactants the solution was exposed by synchrotron radiation. The EXAFS, QEXAFS (EXAFS with faster detection) and XANES transmission spectra of the solutions were recorded at the Au-L_3 edge every constant period of time.

3.4. Results

The overall redox reaction between gold(III) chloride complex ions and ethyl alcohol is known, and can be described as follows:

$$4HAuCl_4 + C_2H_5OH + 3H_2O \rightarrow 4Au \downarrow +16HCl + 2CO_2 \quad (2)$$

However, this reaction can take place in alkaline solution only. In such conditions it is impossible to use spectrophotometry as the experimental technique due to the fact that both of reactants does not absorb photons (electromagnetic radiation) in UV-Vis range. Moreover, it is also incapable to track the fast reaction. Such difficulties can be partly overcome by using the XAFS technique. Figure 4a shows a time evolution of XAFS spectra collected during the reaction of gold(III) reduction. It can be easily observed that XANES spectra collected during the reaction change both: shape and intensity (edge step). Compared with the initial (at 0 s) spectrum of gold(III), they reveal a disappearance of the "white line" as well as a decrease in the edge step intensity. The former change is attributed to the reduction of gold(III) ions, while the latter to the decrease in the concentration of gold species in the solution, also upon sedimentation of the gold precipitate. Comparison of XAFS spectra of solution after reaction to the spectra of precipitate and gold foil (Fig. 4b) reveal almost identical shape, which means that gold complex ions are fully reduced in the solution.
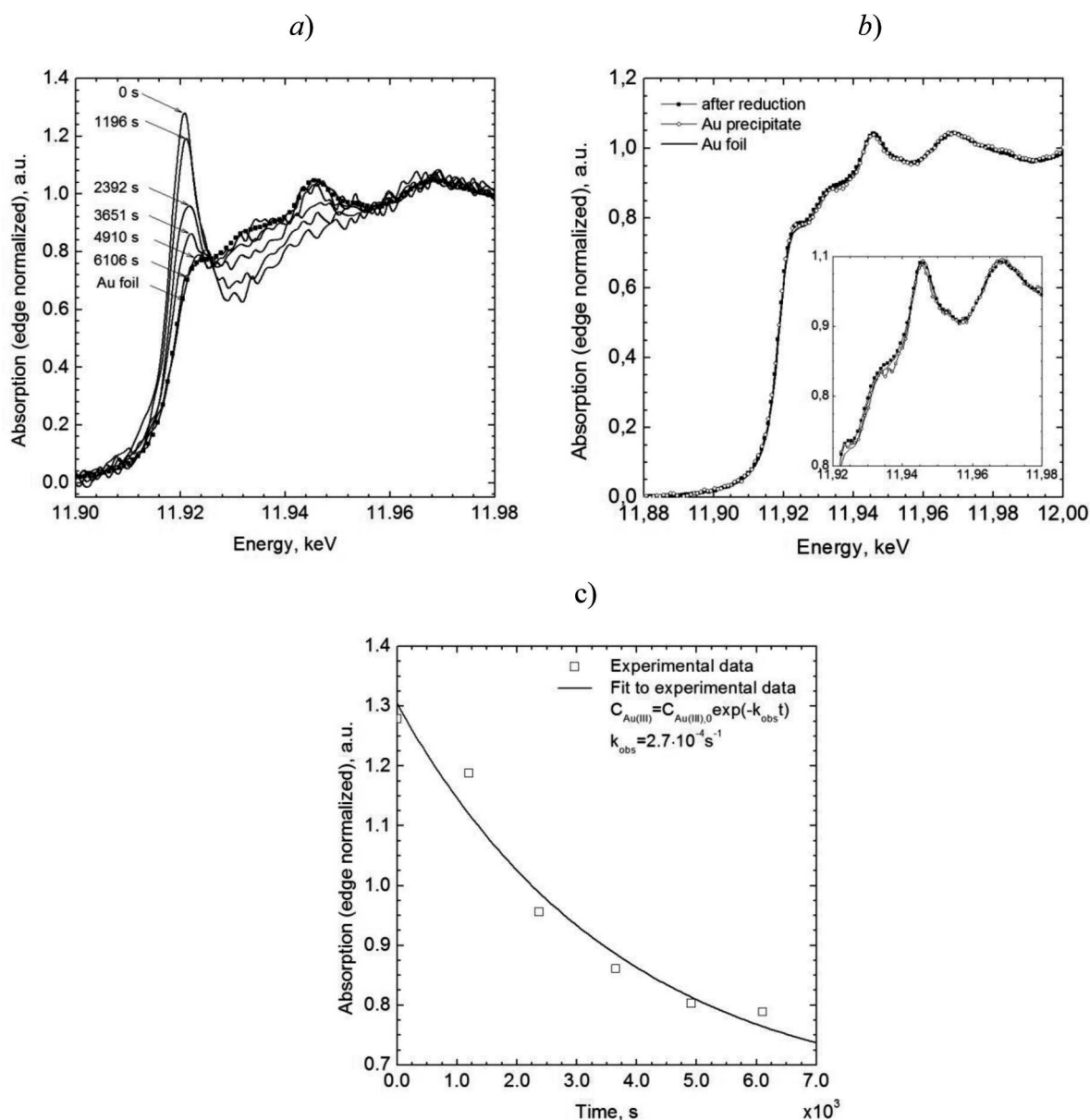
a)

b)

c)

Fig. 4. *a)* Changes in XANES spectra of gold(III) chloride complex ions during the reaction with ethanol; *b)* XAFS spectra of gold(III) chloride complex ions with disappeared "white line" after redox reaction with ethanol; *c)* Kinetic curve obtained from time evolution of maximum absorption intensities (intensity of the "white line") during the reaction. Conditions: pH = 12; temp. = 22.5°C, $C_{0,Au(III)} = 5 \cdot 10^{-3}$ M; 96% ethanol: water (1:1)

Another valuable information which can be obtained from the analysis of the spectra taken during reaction is evolution of the maximum absorption intensity (*I*) at the absorption edge region versus time. From these changes the kinetic curves (changes of *I* vs. *time*) of the studied reaction can be drown in a straightforward way. An example of such a curve is given on the Fig. 4*c*.

For collection of mechanistic as well as kinetic information from the synchrotron measurements also continuous flow technique [23] was applied with the hope of intermediate form of complex ions detection during the reaction. In these experiments, different flow rates of reacting solutions corresponded to different progress (τ) of reaction were applied. Obtained τ were relatively short (milliseconds) as compared with the values reached in the classical methods (minutes). An example of XANES evolution at different times of reaction is shown in Fig. 5.

Obtained results show significant differences in spectra acquired after different time from the beginning of reaction. The disappearance of the "white line" with subsequent changes in the shape of neighbouring registered bands can be observed. These changes suggest the strong evolution in the conformation of the gold(III) complex ions during the reaction. It is worth to mention, that combination of XAFS method with dispersive X-ray optics might allow of probing even faster reactions – in the microseconds range [23].
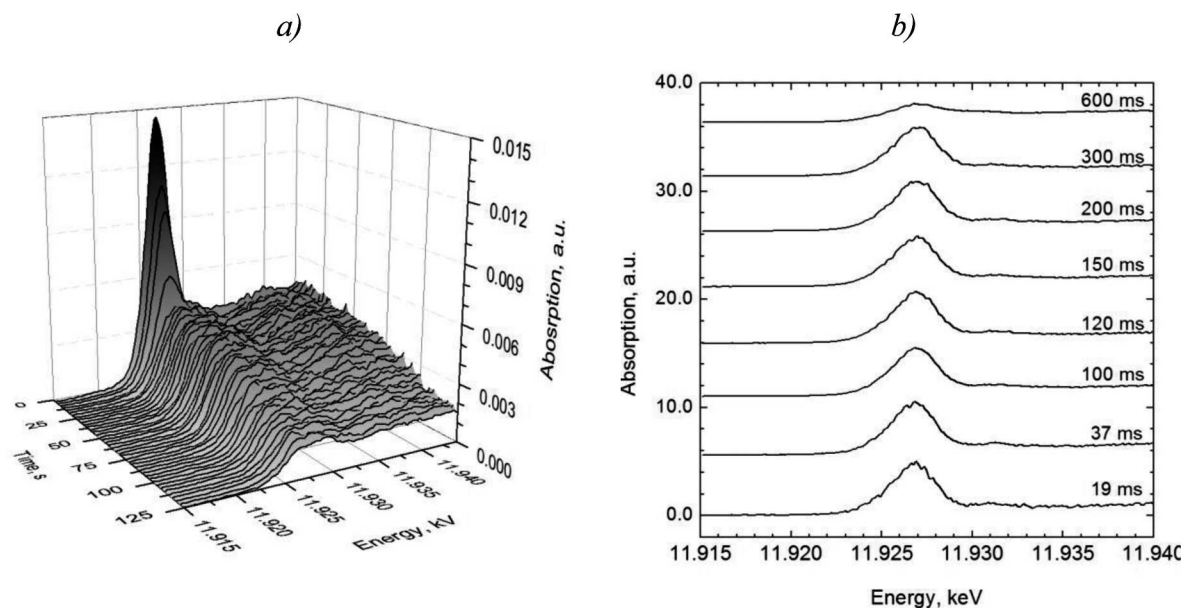
a)

b)

Fig. 5. Evolution of Au L_3-edge XANES spectra of gold(III) chloride complex ions during the redox reaction with ethanol collected over entire reaction (*a*) and within first 600 ms (*b*). Measurements were acquired with application of continuous-flow technique (different flow rates of reacting solution correspond to the different times (τ) of reaction). Conditions: pH = 12; temp. = 22.5°C, $C_{0,Au(III)} = 5 \cdot 10^{-3}$ M; 96% ethanol: water (1:1)
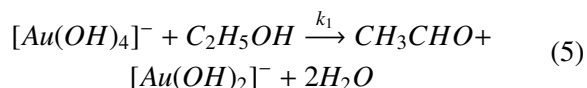
4. Discussion

The form of equation fitted to the kinetic curve (see the legend on Fig. 4*c*) suggests that corresponding differential form of that equation should be described by:

$$-\frac{dC_{Au(III)}}{dt} = kC_{Au(III)} \qquad (3)$$

that is characteristic for a first-order reaction. Taking into account isolation conditions (large excess of reductant applied in the studied system), in fact the equation (3) describes pseudo-first-order reaction and k_{obs} (observed rate constant) is equal to:
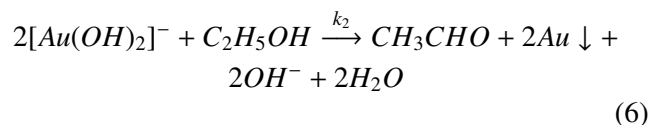
$$k = k_1 C_{ethanol} \qquad (4)$$

Consequently, taking into account that reaction takes place in alkaline solution (in such conditions hydrolysed forms of gold(III) complex ions are present in the system [24]), the first elementary step of reduction reaction can be suggested as:
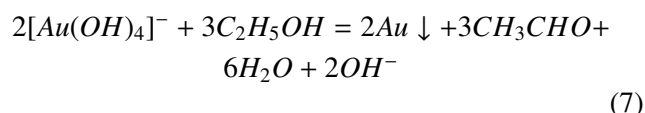
$$[Au(OH)_4]^- + C_2H_5OH \xrightarrow{k_1} CH_3CHO + [Au(OH)_2]^- + 2H_2O \qquad (5)$$

Disappearance of the „white line" in XAS spectrum (Fig. 4*a* and Fig. 5*a*) indicates the change of the valence state of gold central atom from 3+ to 0 in the gold(III) complex ions. Additionally, comparison of XAFS spectra after reduction (Fig. 4*b*) with the Au foil confirms the presence of metallic phase of gold in the system. Taking

into account equation (5), the appearance of gold in the system can be described as the result of reaction:

$$2[Au(OH)_2]^- + C_2H_5OH \xrightarrow{k_2} CH_3CHO + 2Au \downarrow + 2OH^- + 2H_2O \qquad (6)$$

The sum of equations (5) and (6) gives the overall reaction:

$$2[Au(OH)_4]^- + 3C_2H_5OH = 2Au \downarrow + 3CH_3CHO + 6H_2O + 2OH^- \qquad (7)$$

Comparison of equations (2) and (7) indicates the difference in stoichiometry (from 4:1 to 1:1.5) as well as in the form of gold(III) taken to be reduced (eq. (7) gives consideration on the hydrolysed form of gold(III) present in the system).

Summarizing the results obtained from synchrotron studies one can put forward the statement that this scientific tool can be valuable for studies of reaction kinetics under conditions which do not allow application of e.g. spectrophotometry UV-Vis and give the chance to determine the kinetic equation of gold(III) complex ions reduction in alkaline solution.

Another information which can be extracted from XAFS is the confirmation of the structure of gold(III) ions before the reaction in alkaline solution. This form of gold(III) in higher pH was suggested in our previous study [21].

To consider the possible form of the intermediate structure of reacting species and to compare them with

the registered XAS spectra at first, model of gold(III) (Fig. 6a) and ethanol molecule (Fig. 6b) were numerically calculated.

From the charge density distribution for ethanol it can be seen that negative charge is located at the area of oxygen derived from hydroxyl group. It was mentioned

that this region can be a potential area, which is attracted by Au^{3+} central ion before the electron transfer (Fig. 7a). Another possibility of intermediate form (tested numerically) is the adduct in which connection between OH^- ligand and hydroxyl group in ethanol is present (Fig. 7b).
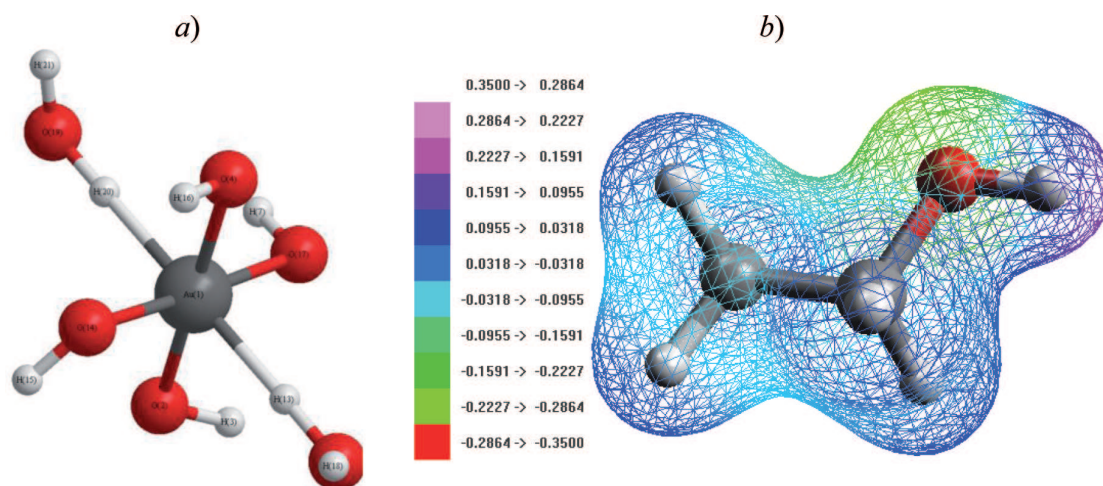
a)   *b*)

0.3500 -> 0.2864	
0.2864 -> 0.2227	
0.2227 -> 0.1591	
0.1591 -> 0.0955	
0.0955 -> 0.0318	
0.0318 -> -0.0318	
-0.0318 -> -0.0955	
-0.0955 -> -0.1591	
-0.1591 -> -0.2227	
-0.2227 -> -0.2864	
-0.2864 -> -0.3500	

Fig. 6. Models of reactants structures: *a*) [AuCl$_4$]$^-$ complex ion in alkaline aqueous solution with coordinated H$_2$O molecules in axial position (experimentally determined from synchrotron measurements [20]); *b*) ethanol with distribution of charge density found from HyperChem 7 calculations
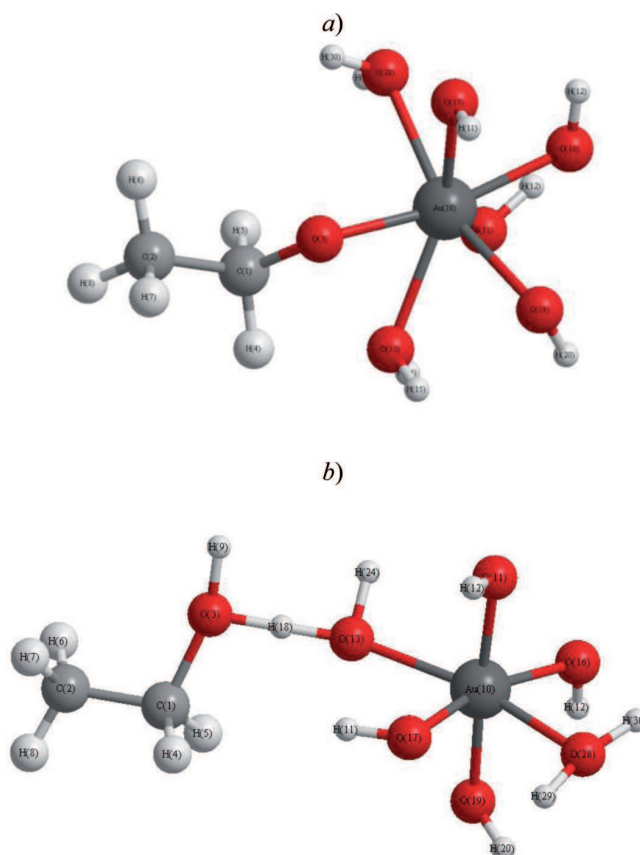
a)

b)

Fig. 7. Two models of possible adducts structure suggesting the way of electron transfer during the reaction between gold(III) complex ions and ethanol: *a*) using Au^{3+} – hydroxyl group bridge; *b*) using OH^- ligand – OH^- group bridge. Calculations were performed using HyperChem 7

With such assumptions, different XAFS spectra were simulated numerically using full-multiple-scattering theory within a muffin-tin potential approximation (FDMNES code [25]) at different distances between reactants. Full multiple scattering calculations were performed for a 5.0 Å radius. Theoretical data were subsequently convoluted with energy dependent core-hole lifetime broadening ($\Gamma_m = 5.0$) and additional Gaussian broadening of 1.2 eV in order to account for resolution of the experimental setup. An example of comparison of XANES spectra generated numerically with that obtained empirically at different time of reaction is shown in Fig. 8. From these results it can be concluded that the resemblance of calculation to the experiment is not far from being satisfactory. Calculated spectrum reveals the similarity with the "white line" intensity of intermediate to this observed experimentally at ca. 25 ms after reaction triggering an corresponds to the structure from Fig. 7b. In spite of lack of the resemblance in the post "white line" spectral shape, the qualitative evolution of the main spectral features in the calculated spectra follows the trend observed in the experiment. This approach seems to be promising as a direct tool to find and suggests the structure of an intermediate species during the redox reaction between hydrolysed gold(III) complex ions and ethanol in aqueous solution.
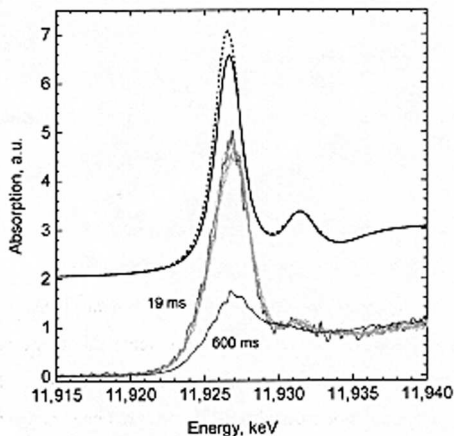

Fig. 8. Comparison of numerically calculated XAFS spectra (black, solid and dashed line) of intermediate adducts from HyperChem calculations (see Fig. 7a and 7b) with empirically registered spectra (grey lines) during reaction of $[Au(OH)_4]^-$ with ethanol

5. Conclusions

1. In situation when the classic methods, e.g. UV-Vis spectrophotometry, cannot be applied to studies of kinetics of reactions in aqueous solution, the unconventional techniques can be used. Among them, XAFS, a technique that utilize the synchrotron radiation, seems very promising.

2. From the intensity of the "white line" in registered XANES spectra during reaction of gold(III) complex ions with ethanol in alkaline solution, the changes in the valence state (from "3+" to "0") of the Au central atom of reacting complex was determined. Such a result confirms that ethanol is efficient reductant of gold(III) complex ions in such conditions.

3. Empirical XANES spectra and changes of absorption intensity characteristic to the small range of energy at "white line" during the reaction give the chance to register the kinetic curve and to determine the rate constant of reaction. The reaction is relatively slow (second-order rate constant k = $3.66 \cdot 10^{-5}$ M^{-1}s) and lead to the gold metallic phase formation.

4. The application of continuous-flow method give the chance for shortening of the changes registration in XANES spectra to the *ms* scale. From the obtained results, supported with numerical calculations, intermediate structures of possible adducts appearing prior the electron transfer can be suggested.

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