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XANES Registration by Electron Beam Position Scanning for Time-Resolved Experiment

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Abstract: A new method of XANES registration has been designed and realised at VEPP-3. Traditionally, the monochromator rotation is used for the energy scanning. In this new method, the position of the monochromator is fixed, but the position of the electron beam is changed by the magnetic field. As a result, the angle SR-beam/monochromator is changed thus changing the energy of the monochromatic beam. We registered test-XANES spectra of Ag by electron beam position scanning and then used this method to investigate fast Ag reduction from organometallic compounds. Depending on the type of monochromator and on the energy interval, XAFS spectra may be measured now within 6-20 s. Traditional QEXAFS has a natural limit, depending on the mass of the crystal of the monochromator, holder and translation stage. The mass of the electrons in the bunch is very small and there is no limit for fast scanning. The use of an undulator as synchrotron radiation source can improve the time resolution of this method by several orders of magnitude and reach nanosecond region.

1. INTRODUCTION

QEXAFS technique for X-ray absorption measurements of time-dependent processes was developed a few years ago [1]. By continuously slewing a conventional X-ray monochromator, the measured times of less than 1 s for the XANES region and of a few seconds for a whole EXAFS scan can be achieved. The dispersive X-ray absorption spectrometer DEXAFS [2,3] basically consists of an elastically bent triangular single crystal as dispersive element and a position sensitive detector . A few dozen milliseconds can be achieved in this method. Faster time-dependent processes can be investigated neither by QEXAFS technique nor by DEXAFS methods. The first one is restricted by the velocity of the monochromator rotation, the second one is limited by the read-out of the diode array detector. The electron beam scanning method is not restricted by these limits.

2. THE MOVING ELECTRON BEAM AT VEPP-3

The task for accelerator physicists is to scan the vertical angle θ_Z of the SR at the entrance slit without disturbing the coordinate of the SR-beam in the same place. Consequently, the electron orbit in the point of radiation must be changed so that the ratio $\theta_Z = \Delta Z/L$ be correct. Here ΔZ is the vertical shift of the electron orbit in the point of radiation, θ_Z is the vertical angle of the electron trajectory in the point of radiation and the entrance angle of the SR beam in the slit system, L is the distance from the wiggler to the slit system. This condition can be realised if an orbit is deformed by two correctors located near the point of radiation and at a distance of $\pi/2$ on phase of the betatron oscillation. It is desirable to make local orbit distortion, compensating a wave arising from other correctors located farther on from the radiation point.

However, under the particular conditions of the storage ring VEPP-3, the quantity and force of the compensated correctors is insufficient. Therefore, a wave of the orbit distortion spreads all over the ring which results in some unfavourable consequences:

a) The changing interval of the angle θ_Z can be limited not only by local aperture near the point of radiation, but by the narrowest aperture over the whole perimeter of a storage ring.

b) Betatron oscillation frequency shift and increase of a betatron oscillation coupling because of the influence of non-linear fields of the sextuple at large orbit distortions can result in the increase of the vertical beam size and worsening of the spectral resolution of the SR beam after the monochromator. These effects can be reduced if the necessary corrections are made in the coupling coefficient during scanning. The necessary amplitude of the scanning angle θ_Z is determined by the experimental conditions, i.e. by the amplitude of the scanning energy ΔE of the SR.

Amplitude restriction is connected with insufficient aperture of a storage ring in the wiggler region, or in any other place of a storage ring, if a local wave of orbit distortion is created. It is really possible to receive a maximum displacement of an orbit in the wiggler Δz_{max}=+ / -3 mm. Thus a maximum orbit distortion in half-perimeter of a storage ring will be + / -7 mm, and an appropriate vertical angle at L=13 m from the point of radiation up to the entrance slit of the monochromator will be $\theta_{z,max}$=+ / -.23 mrad. Under these conditions, at the average energy of the SR beam E=25 KeV, the scanning range is ΔE_{max}=+ / -0.070 KeV. The energy resolution of a monochromator is connected with the angular spread of the SR, through the entrance slit of a monochromator which depends on the vertical size of the electron beam in the point of radiation. The radial emittance beam at the energy E = 2 GeV is equal to $\varepsilon_x = 3*10^{-5}$ rad *sm . Vertical emittance depends on the factor of the betatron oscillation coupling K_c and can be easily made equal to $\varepsilon_z = K_c * \varepsilon_x = 3*10^{-7}$ rad*sm.

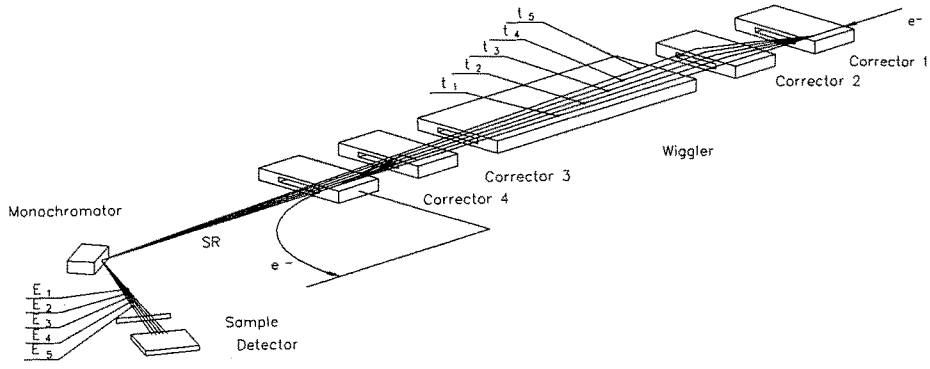

Figure 1: XANES registration by electron beam position scanning at VEPP-3. Originally the monochromator is set up so that it receives the photons from undistorted orbit t_1. Then the orbit is distorted to the maximum deformed orbit t_5 and the scanning procedure begins involving slow changes of the orbit from t_5 to t_1. For each electron orbit, t1- t5 corresponds to the SR beam with the energy E_1-E_5.

The vertical size of a beam in the point of radiation (when the vertical beta function is β_Z=340 cm) is equal to σ_Z=SQRT(β_Z*ε_Z)=0.10 mm. Angular spread of a SR beam in the entrance slit of a monochromator with the width of d=0.1 mm, is equal to $\Delta\varphi_Z$=+/- (σ_Z + d/2)/L = +/-0.012 mrad. Dynamic changes of the scanning procedure are shown on Fig.1. Originally the monochromator is set up so that it receives the photons from the undistorted orbit t_1. Then the orbit is deformed up to the maximum deformed orbit t_5 (Fig.1.) and the scanning procedure begins as the slow change of the orbit from t_5 to t_1 with N steps (usually N=50-:-150 for one scan) and then back to the orbit t_5 with the same number of steps. All the measurements during one step at the EXAFS station were made with ion chambers. After all the scans, the orbit quickly comes back to the undistorted state (orbit t_1).

3. TEST EXPERIMENT

The XANES measurements were performed at the EXAFS beamline of the VEPP-3 storage ring at the SSRC of the BINP, Novosibirsk. The electron beam energy was 2 GeV and the maximum stored current 100 mA. The synchrotron radiation from a 2T wiggler was monochromatized with a single-crystal Si (111) channel-cut monochromator.

Control systems of storage ring VEPP-3 and experimental SR-station are based on CAMAC-embedded microcomputers. For the synchronisation of the process of orbit management controlled by the computer-I with the experimental station controlled by the computer-II, the serial terminal ports of these computers are used. In view of restrictions on the speed of magnetic system reorganisation, the rate of transmission between the computers nearly 1 Kilobyte/sec has appeared quite sufficient for this synchronisation.

Ag foil was chosen for the test experiment. This choice was stipulated by the fact that the K-edge of absorption is 25 KeV, therefore, for the scanning within the energy range of 150 eV, a small angle range is necessary which can be realised at VEPP-3. To scan the range near the K-edge of Cu, a larger aperture would be required. This cannot be realised at VEPP-3. The XANES spectrum obtained by scanning of the electron beam is not worse in quality than the spectrum obtained at the EXAFS beamline by traditional way. Nevertheless, some differences are observed. The main one is the non-linear energy scale of the spectrum. It is associated with non-linear dependence of the magnetic field on the electric current in the correctors. The effect of nonlinearity is most vividly displayed at the saturation of magnets. We used the procedure of energy scale calibration for the corrections of nonlinearity.

4. CALIBRATION PROCEDURE

For the correction of non-linear effects, we carried out the calibration procedure. Calibration involved the following: 1) the current was set with an amplitude provided for staying in the first point E_1 of scan of the XANES spectrum, 2) then, with the help of the EXAFS spectrometer, a spectrum of silver near the K-edge was scanned, 3) the current in the correctors was changed so that it allowed to stay in the second point E_2 of a XANES-spectrum, 4) then, with the help of the EXAFS spectrometer, the shift of the spectrum of silver near the K-edge and the difference $\delta E=E_1-E_2$ were determined. In this way, XANES spectrum was obtained for the whole current amplitude in the correctors, and δE_i for each step of scanning was obtained. So, we found an excellent accordance between the current in correctors and the energy of the SR.

5. TIME-RESOLVED EXPERIMENT

The reduction of silver from silver stearate AgSt + Red -> Ag + HSt was used as the process to be investigated. This reaction takes place in a wide temperature range 70°C - 110°C. The rate of the reaction is temperature-dependent, and the

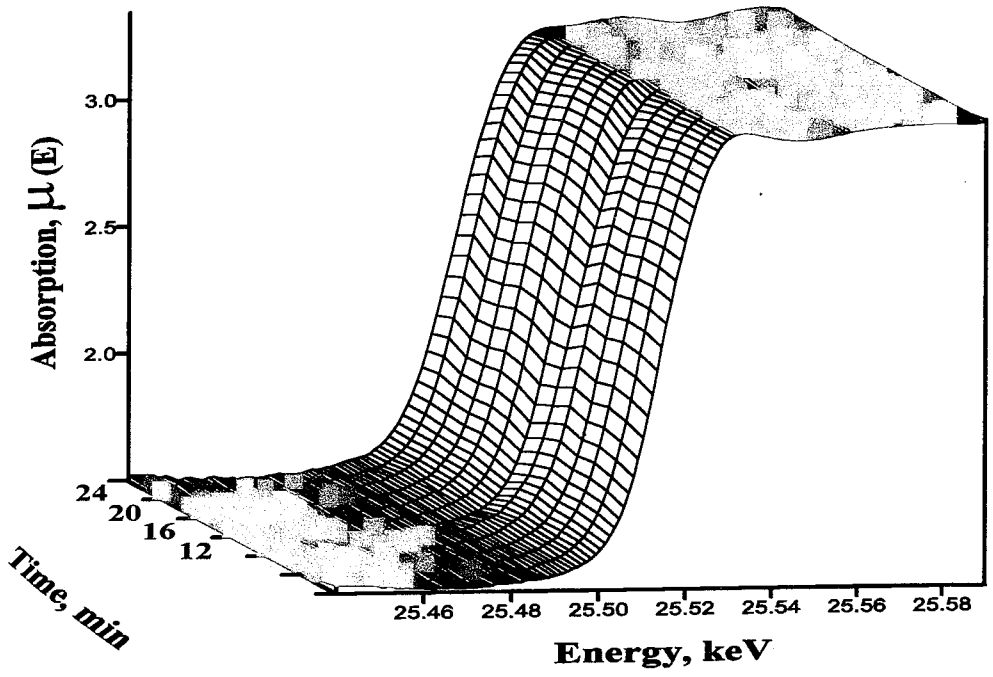

Figure 2: Evolution of the x-ray fine structure near Ag-K edge for the reaction : AgSt + Red -> Ag + HSt at T=80°C.

reaction takes place within the time interval from several seconds up to several minutes. The reaction was conducted under isothermal conditions at various temperatures. Time dependences of the obtained spectra are shown in figure 2.

6. PROPOSAL FOR THE 1000 POLE UNDULATOR

The experiments on VEPP-3 were carried out to demonstrate the basic advantages of the new method. Practical use of the method on VEPP-3 is extremely hindered because of the absence of complete compensation of the orbit disturbance and insufficient aperture of vacuum chamber for electron beam scanning. Both these restrictions are eliminated by the development of special insertion devices aimed at the use of the new method.

The main requirement imposed on these insertion devices is a complete compensation of the local orbit disturbance occurring during the scanning of XANES spectra. At the BINP we have experience in manufacturing such insertion devices e.g. a prototype of an undulator with circular polarisation installed at the NSLS (Brookhaven) and a second one, made for the APS (Argonne National Laboratory). The second requirement is the wide spectral range accessible for scanning. The particular realisation of the offered proposals should be strictly bound to a particular storage ring at which it would be realised. For example, a 1000-pole undulator with a length of ~ 30 m will be established at the SPRING-8. The natural energy resolution achieved at this undulator will be $\Delta E/E \sim 10^{-3}$. Naturally, such a spectrum cannot be used for XAFS. The spectrum should be essentially wider. We present two proposals how this problem could be solved.

6.1 Proposal-1

The basis of the new proposal is very easy to understand from the figure 3: the two correctors (1 and 2) with very rapidly varying magnetic field are used to change the electron orbit so that the trajectory of each bunch is parallel to the stationary electron orbit (t_1). The full scan of the magnetic field in the correctors will take place during ~10^{-8}-10^{-6} s. The other two correctors (3 and 4) are used for the compensation of the overall orbit disturbances from the first and second correctors.

We propose a new design of the undulator with variable field, the gradient of which is perpendicular to the trajectory of the electrons. Since the undulator radiation energy is $E \sim H^2$, (here H is the magnetic field), if we wish to obtain the radiation energy from two extreme trajectories in the undulator (in figure 3, these are designated as t_1 and t_5) differing by 10 %, it would be enough to have a difference in the field in extreme lateral points of the undulator of several percent. Each electron bunch in the undulator has its own trajectory, then each bunch has its own SR beam, which moves in the same way. SR beams diffracted from a "sharpening" bent monochromator will have the energy resolution $\Delta E/E \sim 10^{-4}$-10^{-5} for each bunch. At the same time, each bunch will have its own energy. The SR beam is passed through the sample and registered by a detector.

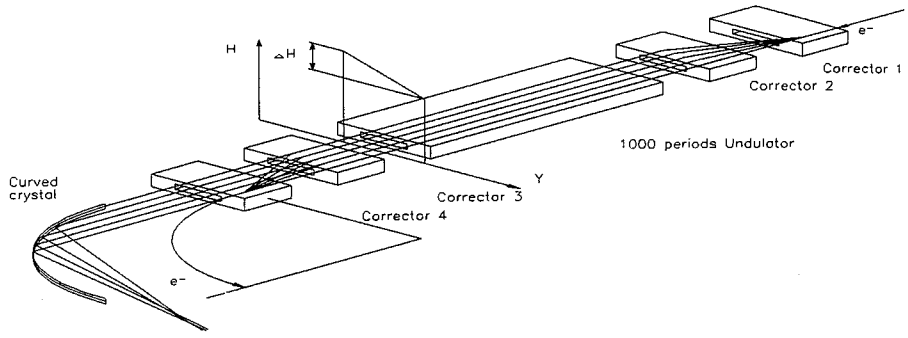

Figure 3: The proposed scheme for the XANES registration by electron beam position scanning at 1000 pole undulator with variable field, the gradient of which is perpendicular to the trajectory of the electrons. SR beams of different energy correspond to each electron orbit.

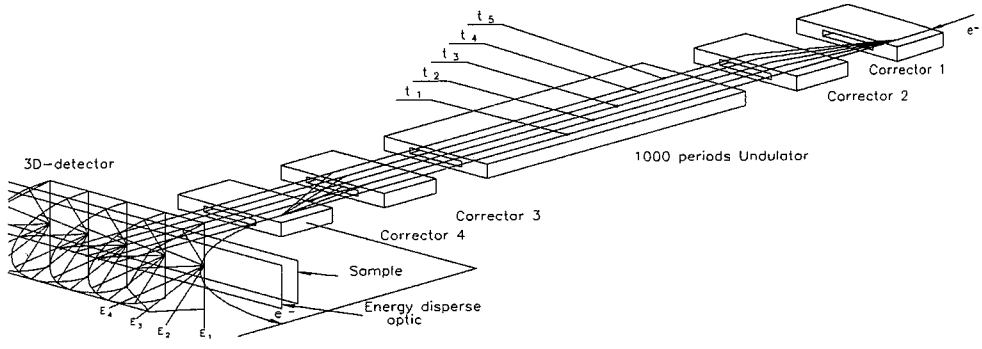

Figure 4: The proposed scheme for the XANES registration by electron beam position scanning at 1000 pole undulator with a variable phase shift. Each electron orbit corresponds to the SR beam which, in turn, corresponds to different time. A SR beam from each bunch diffracts from energy-dispersive elements, passes through a sample and then is registered by its own linear detector (one detector for each bunch). Thus, the magnetic field scan in the correctors is the scan in time.

Thus, the magnetic field scan in the correctors is the energy scan at the same time. Distance between bunches is the factor defining time resolution of the XANES registration. For example, if the time between two bunches is 5 ns, then time resolution is 500 ns for one spectrum.

6.2. Proposal-2

It is rather easy to distort the phase of radiation from various elements by phase shifters or by varying the undulator parameter K to spread the radiation spectrum. In this circuit, energy dispersive elements and linear detectors can be used to obtain EXAFS spectrum within one bunch. In this circuit it is not necessary to scan energy, since it is executed by energy dispersive elements. Therefore, the circuit of a moving source of the SR can be used for another purpose, namely, for time scanning. The basis of the proposal is the undulator (Fig.4.) with varied electron orbits where each bunch has its own trajectory. The SR beam from each bunch diffracts from energy-dispersive elements, passes through the sample and then is registered by its own linear detector (one detector for each bunch). Thus, the magnetic field scan in the correctors is at the same time the scan in time scale. Distance between bunches is the factor defining time resolution of the XANES registration. For example, if the time between two bunches is 5 ns, then the time resolution is 5 ns for one spectrum.

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