Template for MAX IV Expressions of Interest (Draft v5)

Administrative section

Which type of EoI are you submitting (tick one):

☒ Complete beamline

☐ Experimental stations, instrumentation, or upgrade

☐ Other infrastructure and capabilities: [If Other, please enter a brief explanation here]

Title of EoI:

Tender and Hard X-ray beamline for X-ray Spectroscopies

Acronym or short name:

HAPPY: HArd Photon Photoemission

TEXPES- TEnder X-ray sPectroscopiES

TEXMEX- TEnder X-ray Multi EXperiment beamline

TEXMax – TEnder X-ray beamline at MAX IV

SPUTEX- SPectroscopies Using TEnder X-rays

Branchline Names: Kai (HAXPES) and Manne (XES/XAS/RIXS/Raman)

Additional information (required)

Is there already a Conceptual Design Report or similar?

☒ NO ☐ YES – If yes, please provide a link to document here: [Enter URL]

Does the EoI relate to any areas mentioned in the MAX IV Strategy? (multiple choice)

Transformative Science areas	Cross-Cutting topics
☒ Health and Medicine	☐ Imaging
☒ Tackling Environmental Challenges	☐ Dynamics
☒ Energy Materials & Technologies	☐ Data analysis, Machine Learning and AI
☒ Quantum and Advanced Materials	
☐ Ultrafast Science	☒ Other
☒ Accelerator Science	Low Density Matter

Is the intended item already funded?

(most should tick no here, unless funding is already approved)

☒ NO ☐ YES – If yes, by which entity? Enter organisation

Is there any cross-dependence between this EoI and others?

☒ NO ☐ YES – If yes, which one or ones? Please specify

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Abstract

We propose to build a high-resolution **tender and hard x-ray spectroscopy beamline** in the energy range of 2-20 keV. The primary application of the beamline will be photoemission and X-ray based spectroscopies (x-ray emission, absorption, inelastic scattering, and Raman spectroscopies) on complex materials under vacuum, *in situ* and *operando* conditions. The proposed beamline will provide state-of-the-art and workhorse capabilities for the Swedish research community within both academia and industry in such fields as Catalysis, Low Density Matter, Atmospheric Chemistry, Atomic and Molecular Physics, Photovoltaics, Energy Storage, Nanodevices, Electrochemistry, Corrosion, and many others. It is clear from the information obtained by the working group while preparing this Expression of Interest that the demand for such facility at MAX IV by the Swedish and international communities is tremendous. The technical capabilities and the expertise present in the lab can ensure the success of such project. Moreover, the successful implementation of the goals presented in the Energy Materials and Technologies, Tackling Environmental Challenges, Quantum and Advanced Materials, Low Density Matter, and Industry Relationships sections of the ongoing MAX IV Strategy 2030 is clearly and strongly dependent from the immediate access to the tender and hard x-ray spectroscopy methods. We, therefore, think that it should be of primary MAX IV importance to ensure the proposed project is prioritized within the roadmap and supported in the process of seeking future funding.

Background

The Swedish research community has a deep-rooted tradition in X-ray spectroscopies, both photoemission and X-ray emission. This is reflected in the rich portfolio of X-ray spectroscopy beamlines previously established at MAX-lab and now operating at MAX IV. The tender/hard X-ray spectroscopy has been established at many synchrotron facilities and now belongs to the standard state-of-the-art and workhorse techniques for material characterization. The overwhelming demand from the academic and industrial research communities within Swedish and abroad strongly motivates a realization of a high throughput tender and hard X-ray spectroscopy beamline in Sweden for applications in atomic, molecular, chemical, and material sciences. The technical capabilities of the MAX IV 3 GeV storage ring and available expertise in the lab warrants a successful implementation of such project.

HAXPES and tender/hard X-ray emission spectroscopy are important techniques which provide access to sub-surface and bulk material properties, buried solid-solid and solid-liquid interfaces, solid-gas interfaces at atmospheric pressures, molecules and catalysts in solution and quantum materials. The methods have been applied to many scientific areas ranging from fundamental atomic, molecular, and condensed matter physics, electrochemistry and surface/interfacial science to technologically important areas such as (electro-, thermal, photo-) catalysis, energy storage materials, fuel cells, photovoltaics, and electronic devices. The methods benefit greatly from synchrotron radiation due to its high brightness, tunability, energy resolution, and small beam sizes.

Hard X-ray photoemission and X-ray emission spectroscopies are now standard methods offered at all major synchrotrons, including multiple European facilities. Applications of these techniques are currently strongly growing with numerous beamlines and instruments starting operation and being developed at the 3rd generation synchrotron facilities (ESRF, Soleil, BESSY II, PETRA III, Swiss Light Source, Diamond, SSRL) and X-ray free-electron lasers (SwissFEL, Switzerland, and PAL FEL, Korea).

The advent of the 4th generation storage rings brings new possibilities for tender/hard X-ray spectroscopy: smaller emittance will result in the increase of the spectral brightness and resolution as well as the decrease in beam size. This, combined with the advances in detector development, will push the temporal resolution of the techniques. When incorporated with various in situ and operando sample environments (photo/electrochemical cell, liquid jets etc.), tender/hard X-ray spectroscopy addresses all three complexity domains for a given system – chemical/compositional, temporal, and spatial domains. This was also highlighted in the recent review of the HAXPES technique which discussed state-of-the-art in 2020 [1] (and it is true as well for tender/hard X-ray emission spectroscopy). It is remarkable that the authors of this review specifically mentioned MAX IV in the article text as the first 4th generation synchrotron but could not elaborate further due to lack of HAXPES facilities at the Swedish synchrotron. This example clearly indicates that both scientific communities – users and instrument scientists – see HAXPES as a natural development for MAX IV and expect that Sweden joins the community as soon as possible.

Scientific Case

Atmospheric Chemistry and Environmental Challenges. *Atmospheric, and Environmental chemistry* are areas where tender and hard x-ray-based spectroscopies are indispensable. Understanding of the novel Surface-Promoted RedOx (SPRO) mechanism [2] is especially important in the context of Atmospheric Chemistry**.** The use of tender/hard X-ray spectroscopy will first allow the crucial access to K- and L-edges of the halogens. Second, with the increased probing depth it becomes possible to probe the nature and dynamics of the chemical transformations induced by atmospheric trace gases and aerosols, ice particles, or water droplets. These problems are directly relevant to the problems of climate change, ozone hole formation, and changes in the weather patterns. The new beamline will complement the existing APXPS beamlines at MAX IV – HIPPIE and SPECIES.

Low Density Matter, Life Science, and Medicine. X-rays in the tender and hard range provide access to deep-lying s-, p- and d-levels of a majority elements in the periodic table. New insights into rapid nuclear dynamics emerge as deeper inner-shell levels are accessed, and shorter electronic state lifetimes in the attosecond range illuminate fragmentation, charge distribution and recoil effects in molecules [3]. Primary questions include distribution of the absorbed energy by the high-Z atom among nuclear and electronic degrees of freedom, and the relative time scales for competing processes [4]. A profound knowledge of such decay processes is very important in pinpointing mechanisms central for *plasma physics and astrophysics*. In *radiation biology, x-ray crystallography and single particle imaging* site selective x-ray induced fragmentation of large biomolecules is of primary interest. These molecules are typically built up by light elements such as carbon, oxygen and nitrogen, but many proteins also include e.g. sulfur and phosphorus. At high x-ray energies S and P have a higher photoionization cross section than the lighter elements and will therefore act as a hot spot for radiation induced fragmentation which leads to protein damage [5]. It is therefore necessary to study the fragmentation that occurs after ionizing at the sulfur and phosphorus K-edges (at 2. 47 keV and 2.15 keV respectively). Relevant low density matter experimental setups are available at MAX IV.

Energy Materials and Technologies. Increasing the probing depth of HAXPES to 10-50 nm in the hard X-ray range is a game changer for investigations of many electrochemical systems such as *batteries, artificial photosynthesis, dye-sensitized solar cells, and electrocatalysts*. The performance, stability, lifetime, activity, and selectivity of these systems are governed by the characteristics of the solid-liquid interfaces. For example, for batteries, understanding of the SEI - a thin (2-40 nm) passivation layer formed on the anode due to electrolyte decomposition – is crucial to obtain high-energy-density batteries. In addition, due to the higher information depth of HAXPES it can be used to access the redox active material beneath the interface and electrolyte layer and follow the material properties during lithiation/delithiation also during operando cycling, since the electrolyte can be kept thick enough to properly conduct current [6]. The benefits are true for the modern Li-ion systems but will also remain of critical importance for most of the future systems based on the novel electrode materials (Na, K, Al) [7] and electrolytes (traditional organic, ionic liquids and solid membranes) [8].

Nearly all processes involved in the energy conversion are based on the *thermal catalytic transformations* and thus strongly dependent on the properties of the interfaces between solids and gases. In addition to the existing soft X-ray APXPS beamlines at MAX IV which are capable of studying catalytic processes in the mbar regime and only at the surface a future tender and hard x-ray capability would enable studies at much higher pressures (up to atmospheric and above) due to the large inelastic mean-free path of the high energy electrons and X-rays [9]. Reaching such conditions in an experimental setup is critical for a large number of catalytic processes where the product formation can only be observed at the industrially relevant pressures in order to settle pressure gap debate. Furthermore, chemical transformations not just at the surface but also within nanoparticles, layered, bulk materials, and membranes become possible to study at higher energies.

For many photo-, thermal- and electrocatalytic systems particular attention must be paid to the methods aimed at uncovering *dynamic nature of the catalytic processes* – from the elementary steps, charge transfer, electronic and nuclear dynamics active species, and transition states (ps-µs) through ion diffusion, solid-liquid chemical transformations, and setting up of the electrochemical potential within electric double layer (µs - ms) to bulk effects such as phase transformations (ms-hrs) [10]. The approach will be to combine operando tools with time-resolved spectroscopies to detect species as they respond to an external stimulus (e.g., mechanical, chemical, pressure, temperature, electrical potential, or optical perturbations). Time resolution of hundreds of picoseconds could be achieved by combining the high brightness of the MAX IV 3 GeV ring with a synchronized optical laser system and

the developments in fast electron and X-ray detection; whereas attosecond time frame will be possible to explore with help of the Resonant Auger Spectroscopy core-hole clock technique [11]. In the long term, new **Accelerator Developments** at the 3 GeV ring might push time resolution to single picoseconds in standard pump-probe experiments.

Industrial Applications. HAXPES is an effective tool for the *in-situ* analysis of surface evolution of metals in contact with different medias, including gases and liquids, topics of particularly high interest to Swedish *metal industries*. For the high-temperature applications the mechanism of initial stages of oxidation, nitridation and carburization are still under debate. Among the aspects needed to be clarified are: (i) the effect of alloy composition on properties of the surface oxides forming during high-temperature treatments; (ii) chemical transformations (dissociation and ion diffusion) of the adsorbed gases and chemical changes in the surface oxide as a function of surface temperature/gas mixture. The area requires taking measurements under conditions relevant to the extreme environments observed in many industrial applications, such as temperatures reaching 700 °C and several bars of corrosive gases. In the field of wet corrosion, the performance of operando electrochemistry studies to understand of the interaction between corrosive media (electrolyte), surface films, and base material is a priority and also here the higher x-ray energies are of high importance.

Quantum and Advanced Materials. Many critical interfaces in the *advanced materials and devices* are buried under one or several thin films, which require a probing depth of a photoemission spectroscopy up to several tens of nm, which cannot be reached using the soft X-ray methods currently available at MAX IV. Sputter etching traditionally used for depth profiling is known to preferentially remove lighter elements as well as to induce sputter damage, therefore for many materials this is not an option. For such multi-elemental materials HAXPES is an invaluable tool due to its non-destructive, non-contact probe, and extended depth profile. This becomes even more powerful with metal K- and L- edge HERFD-XAS and high-resolution XES or RIXS. RIXS will enable measuring the low-energy excitations in strongly correlated solid-state quantum materials and the valence-excited state structure in liquid-state homogeneous catalysts. Spectroscopic measurements must be also possible during real device operation, attributing device performance improvement or failure to specific interface properties [12].

High entropy alloys - solid solutions with at least five elements in a near-equimolar composition – is one example of complex material which exhibit interesting properties such as high strength, corrosion resistance, and high hydrogen storage capacity [13]. Addition of small amounts of light elements is known to strongly affect their properties, but their distribution – at preferred lattice sites, or random - it is not known. ABX_3 *perovskites* is another promising material due to the wide range of ferroelectric, magnetic, superconducting properties. The sub-family of APbX3 lead halide perovskites (HaPs) has shown substantial promise for applications such as solar cells (which are competitive with state-of-the-art Si and GaAs cells), light-emitting diodes, lasers, X-ray and gamma-ray scintillators, and more [14,15,16]. As multi-elemental compounds, substantial insight can be gained with element-selective X-ray absorption and emission spectroscopies [17,18].

Electronic end optoelectronic devices such as those based on the ultrathin oxide films with ferroelectric or resistive RAM properties (which are promising for realizing steep-slope transistors, neuromorphic networks, or memory applications) where the full gate stack consists of a bottom electrode (Si, III-V semiconductors, or metals), the high-k oxide film such as $Hf_xZr_{1-x}O2$, and the top metal electrode are also type of materials that need to be studies with non-destructive method as a whole [19]. This is to distinguish the influence from several materials parameters such as oxygen deficiencies at top or bottom interfaces.

Layered PV materials are probably one of the most complex advanced material systems comprised of a multitude of layers, interfaces, elements, impurities, etc. The critical part in the *thin film solar cells* is the interface between the absorber and buffer layer whose properties depend on the absorber surface band gap widening, distribution of alkali trace elements, and the energy band alignment [20]. For the *organic solar cells*, the additional complexity is introduced by the molecular blend layers wherein the nanostructure, domain separation and purity together with vertical molecular concentration gradients play important roles [21]. Even more, the interface properties are changed during the device processing as a result of sequential deposition of multilayers at different deposition conditions. To ensure continuous performance improvement, detailed insight into the chemical and electronic structure of the operational device is necessary.

The study of the reactions in the *Atomic Layer Deposition*, the method that is often used for creation of complex layered structures [22], itself benefits from the increased information depth when using

higher x-ray energies especially for the systems where the critical ALD reaction occurs at buried interfaces, e.g. when the precursor molecules have to diffuse through thin amorphous films (as of high-k oxides or other functional materials) before reaching the target interface.

User community and engagement

Swedish user groups are engaged in both fundamental and applied research including important research themes in material science, catalysis, photovoltaics, and battery research. For the community, tender/hard X-ray spectroscopies form an important set of techniques that will undoubtedly continue to grow in the future. HAXPES alone has reached around 80 publications per year in 2020 [1]. Approximately 8% of the yearly HAXPES publications includes authors from Swedish universities. Strong HAXPES user groups already exist within Sweden, with the largest ones at UU (Rensmo and Edström) and SU (Nilsson). A Swedish HAXPES beamline at MAX IV would be the ideal catalyst for current Swedish users to start using HAXPES. Hard X-ray emission spectroscopy is a growing field at MAX IV already and extending this to the tender range will create new users at MAX IV that are currently focusing on soft X-ray spectroscopy. One example is the application of X-ray emission spectroscopy (XES and RIXS) to metal L-edges and ligand K-edges (S, P) in actinides and 4d/5d metal complexes (Butorin, Wernet, UU).

The expected increase in Swedish and Nordic scientific output for tender and hard x-ray spectroscopy is clearly reflected in the interest and support for such beamline. Several workshops were held discussing the need for HAXPES in particular by the Swedish community. A meeting in Uppsala held in 2017 about combining diffraction and HAXPES (DiffMAX project) attracted 65 participants. An on-line Tender/HAXPES beamline project workshop with discussions of science cases for HAXPES and tender/hard X-ray emission spectroscopy in June 2021 attracted more than 100 participants. From the discussion at both venues, it is clear that the demand from the Swedish community for tender and hard X-ray spectroscopies is not met at MAX IV. Based on this interest, several new user groups are expected to join the tender and hard x-ray community, covering research areas from atmospheric and life science to industrial R&D in existing steel - and emerging battery companies.

Technical specifications

- Energy range: 2 (or slightly below) keV – 18 keV.
- Light source: IVU with 21 mm period and K_{max}=2.5 similar to the existing CoSAX or MicroMAX devices. I > 10^{20} ps/s 0.1% BW mm2 mrad2 (1-20 keV)
- 4 or 6 bounce high-resolution (channel-cut) monochromator (HRM) to achieve >100,000 resolving power in the whole energy range to achieve <100 meV resolution at the highest energy.
- Two branchlines: for HAXPES and X-ray emission spectroscopies.
- Access to an open port
- A long beamline (80-100 m) might be necessary to create enough spacing between two branchlines. Alternatively, diamond split windows might be used allowing for simultaneous operation of the branchlines albeit with interdependencies in energy.
- Variable beam size with transfocator based on CRLs for reaching beam sizes down to 1 µm.
- Selection of plug-and-play endstation realising following methods and sample environments:
    - Modular detectors and sample environments which are used in different combinations.
    - Use of several detection methods (e.g. HAXPES and XES) in a single experiment
    - HAXPES
        - Both major suppliers of the HEEA showed interest in developing instruments capable of going to 20 keV including ambient pressure versions.
        - (Ultrahigh) vacuum PES including surface science type sample preparation
        - Ambient Pressure PES including sample environments for electrochemistry, (atmospheric pressure) catalysis, and low-density matter studies
    - Emission spectroscopies: XES, (HERFD-)XAS, RIXS, X-ray Raman
        - Access to different types of emission detectors that are not currently present at MAX IV (e.g. von Hamos, Johann)
        - Selection of ready-to-use operando and in-situ sample environments for standardized samples including He environment, electrochemical, catalysis, diamond anvil cell, liquid jets, etc.

- Existing at MAX IV expertise in optical and experimental stations design make us confident the beamline will be finished within 4 - 5 years: 0.5-1 year for detailed optical design; 1.5-2 years for production of the components; 1-1.5 years for installation and commissioning. Cost of the beamline can be estimated based on the cost of typical hard x-ray beamline at MAX IV.

State of the Art / Benchmarking

The development of beamlines dedicated to HAXPES took really off from the early 2000's and the field has grown steadily since then adding one new beamline per year. At the moment, 25 beamlines around the world offer PES with tender and hard x-rays with seven present among European synchrotrons: BM25 (ESRF), GALAXIES (SOLEIL), EMIL, KMC-1 (BESSY II), P22 (Petra III), X07MB (SLS), I09 (Diamond). Tender X-ray emission spectroscopy is being developed at various synchrotron and X-ray free-electron laser facilities. To our knowledge all of these beamlines are heavily used by the Swedish researchers, but significantly oversubscribed, clearly demonstrating the importance of this characterization method to the field of material science.

Among the mentioned above facilities only one of them (GALAXIES) is, to our knowledge, combines HAXPES with other x-ray spectroscopies such as RIXS, XES and X-ray Raman. Only two synchrotrons (Soleil and Diamond) offer high-flux, high-resolution PES facilities in both soft and hard x-ray range. In addition, SLS and HZB offer ambient pressure PES instruments that cover both soft and hard X-ray PES, however, in both cases these instruments struggle to provide both high flux and high resolution.

The proposed project will outperform all currently available European HAXPES facilities in flux or resolution. Also, the proposed endstations and sample environments combined with the access to the existing MAX IV PES beamlines – FlexPES, FinEst, Bloch, Species, and Hippie – will allow studies of systems under wide range of conditions with both soft and hard x-rays within the same facility and thus single beamtime. MAX IV will be one of the few European synchrotrons to allow such possibility for HAXPES and tender/hard X-ray spectroscopy which will attract Swedish and international communities.

Impact statement

The methods offered at the proposed beamline will streamline studies of solid-liquid interfaces in electrochemical systems under operando conditions and will turn the technique into a routine method with endless possibilities for automation and batch sampling. This will lead to substantial increase in the rate of knowledge gained in fields such as energy storage materials, photovoltaics, corrosion, and electrocatalysis for both fundamental and applied studies. PES at real industrial pressures (1 bar and above) will finally put an end to the long-standing debate about the "pressure gap" in catalysis. Increasing of the probing depth in PES to a few tens of nm will open new possibilities to study equilibrium chemical composition of the sub-surface layers in systems such as atmospheric aerosols and ice particles, nano electronic devices, membranes, and solar cells, and complement the already existing PES at surfaces. X-ray emission spectroscopies would be an ideal complement to PES in the tender and hard x-ray range by providing information about electronic structure in addition to chemical information gained from PES, especially if both experiments could be performed in a single beamline (during a single beamtime). Access to the K and L edges of most elements and increased information depth will also make tender/hard X-ray emission spectroscopy a standard tool itself for routine use in chemical and biological sciences and in catalysis. A new suite of x-ray spectrometers (e.g. Von Hamos and Johan) will complement the capabilities of the Balder beamline at MAX IV. The unique property of MAX IV – its low emittance – and hence extreme brilliance will be the key to enable new potentials for tender/hard X-ray emission spectroscopy (unprecedented sensitivity and spectral resolution). The beamline will thus benefit from the future upgrades which will further decrease emittance.

The proposed project intimately relates to several transformative science areas within the MAX IV Strategy, namely Energy Materials and Technologies, Quantum and Advanced Materials, Tackling Environmental Challenges, Accelerator Development, and Industrial Relationships. The chance of reaching strategic goals presented in these sections is critically dependent on the availability of HAXPES and hard x-ray emission spectroscopies at MAX IV in the near future. Without such capabilities available within the time horizon stated in the Strategy, MAX IV might fall behind its European competitors in the areas mentioned above. This would be disastrous since the Swedish research communities are strong in many of these areas.

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Proposers

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The presented EoI is a result of **direct** contributions of all mentioned above authors. We would also like to note generally high interest and support of the proposed project among numerous research groups from all major Swedish universities, research institutions and many industries that can be clearly visible in the private communications with their representatives and through the direct participation in the project-related workshops. The interest of Swedish industries is apparent through the contact with mediator organizations (e.g. SWERIM) or Industry-Academic alliances (e.g. BAttery SWeden).

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