IN COLLABORATION WITH ISOLDE, HISKP AND THE INSTITUT FÜR THEORETISCHE PHYSIK, TU CLAUSTHAL

A PARTICULAR EFG TEMPERATURE DEPENDENCE FOR ^{181}TA(TIO$_2$): AN ELECTRON-GAMMA TDPAC STUDY

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Venue: ISOLDE Workshop and Users‘ Meeting, 2021

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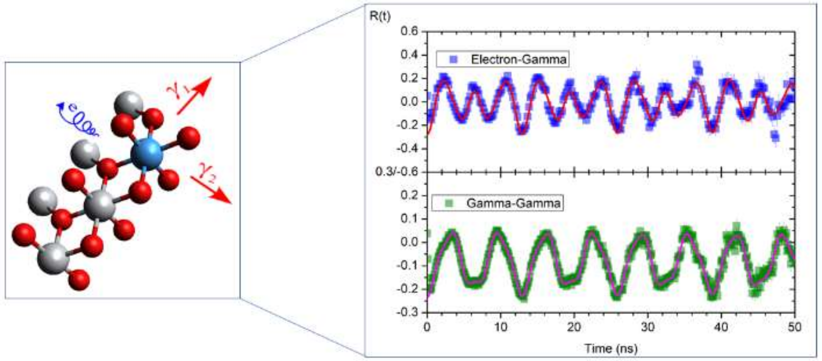

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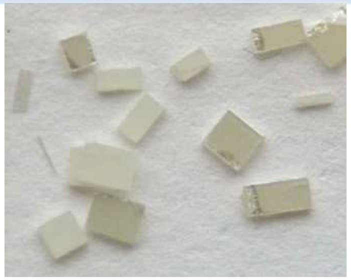
Introduction (Experimental)



Introduction (Experimental):

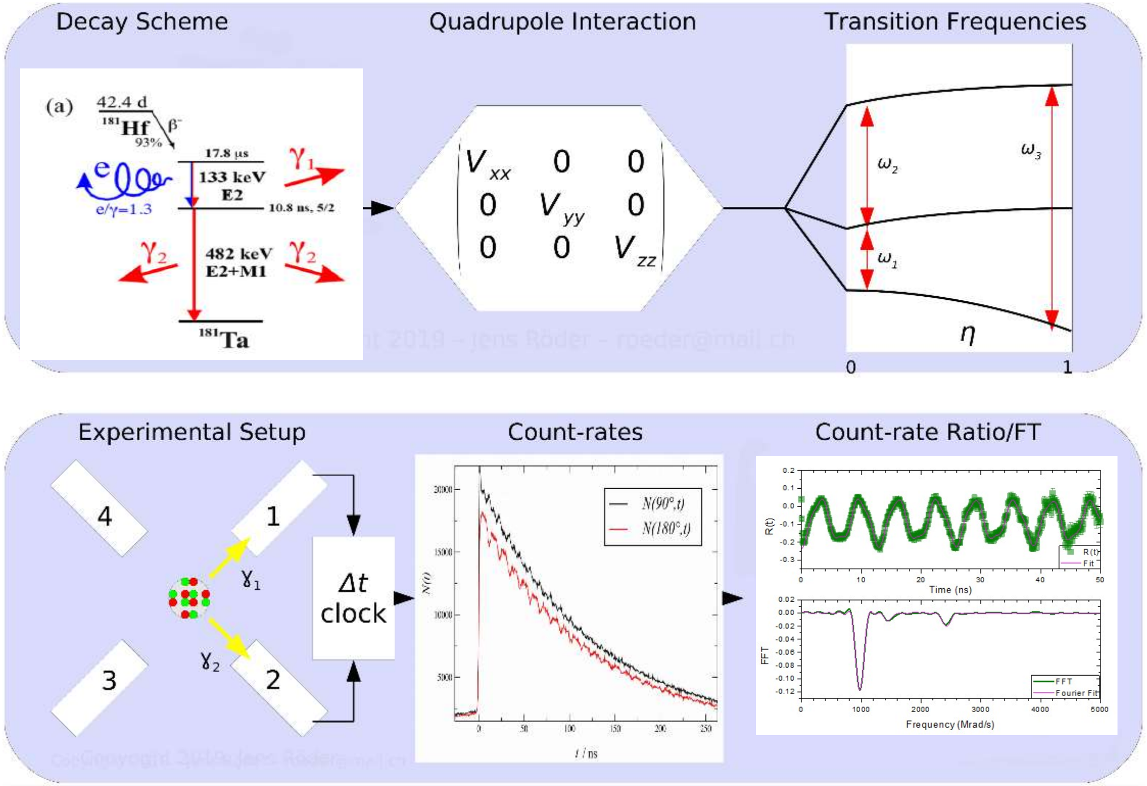
- **Motivation:**
    - To investigate the temperature dependence of the electric field gradient (EFG) surrounding the ^{181}Ta site in TiO_2 using $e-\gamma$ Time-Differential Perturbed Angular Correlation (TDPAC) spectroscopy.
- **Why?**
    - There exist no $e-\gamma$ TDPAC applied to $^{181}Ta(TiO_2)$ (yet).
    - There exist published Room temperature (RT) $\gamma-\gamma$ TDPAC results for $^{181}Ta(TiO_2)$ to compare our $e-\gamma$ TDPAC to.
    - There are low-temperature regions with no TDPAC experimental data for rutile TiO_2.
        - Literature predicts extension of the linear dependence of hyperfine parameters to the low temperature regime.

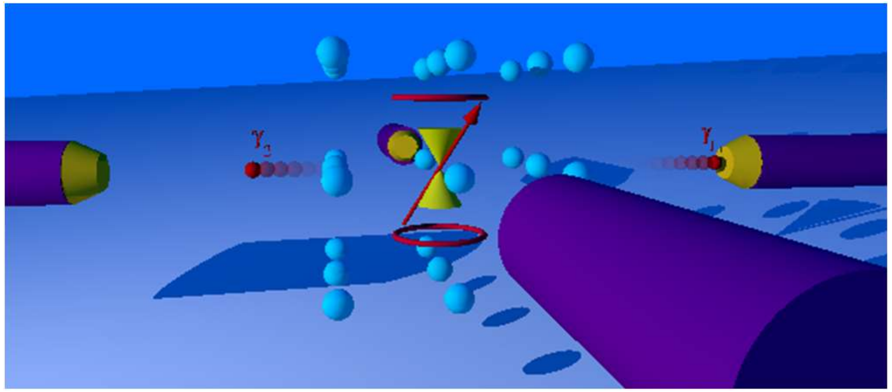
[James 1994]: https://doi.org/10.1103/physrevb.50.1264
[Darriba 2011]: https://doi.org/10.1103/PhysRevB.79.115213

Quick overview of concepts of TDPAC

Concept of TPDAC

Figure adapted from: Jens Röder, “Schema of PAC-Spectroscopy” – Own work, CC BY-SA 4.0, 24/11/2019, Wikipedia Entry: Perturbed angular correlation

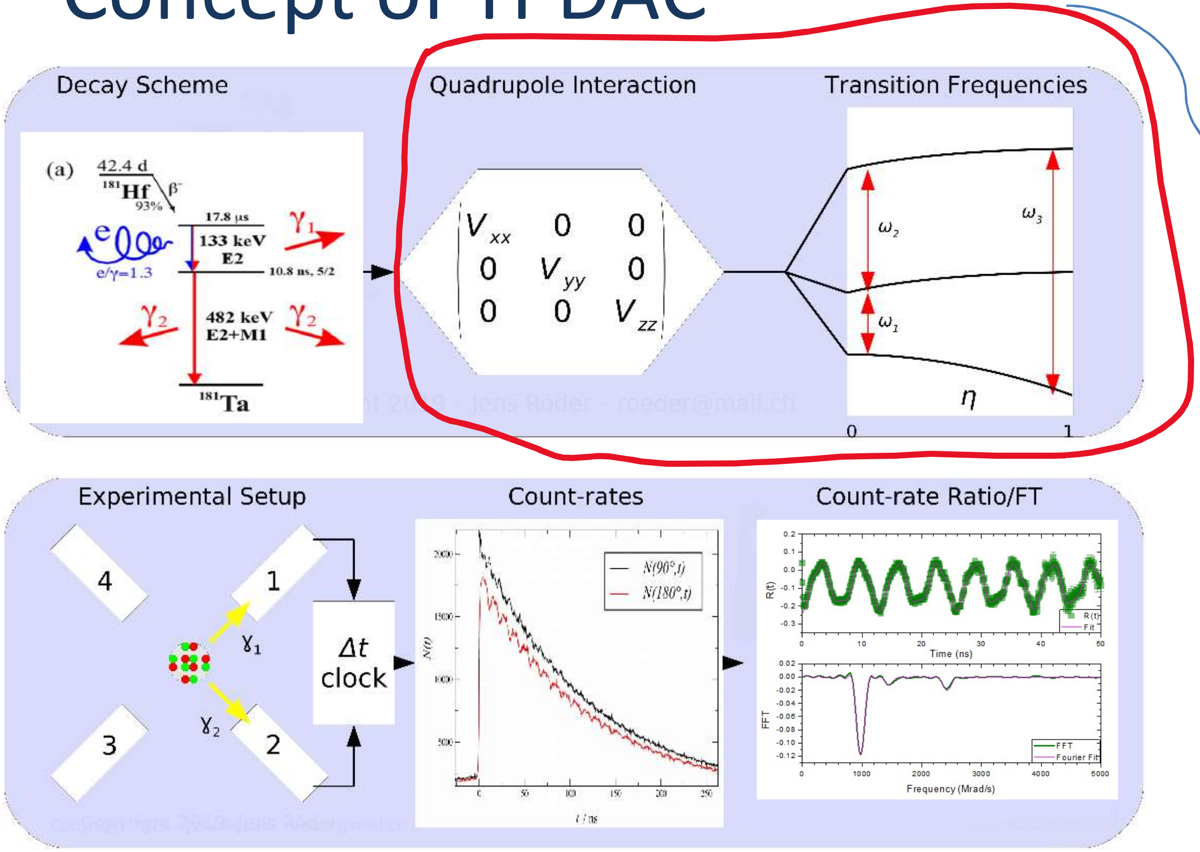




Mathematical details can be found in:
[Butz 1992]: https://doi.org/10.1007/BF02418614
[Schatz, G.; Weidinger, A.]: Chapter 2,5 ISBN 0 471 95479 9
[Steffen, R. M.; Alder, K.]: Chapter 13, ISBN 0 720 40275 1

[James 1994]: https://doi.org/10.1103/physrevb.50.1264
[Darriba 2011]: https://doi.org/10.1103/PhysRevB.79.115213

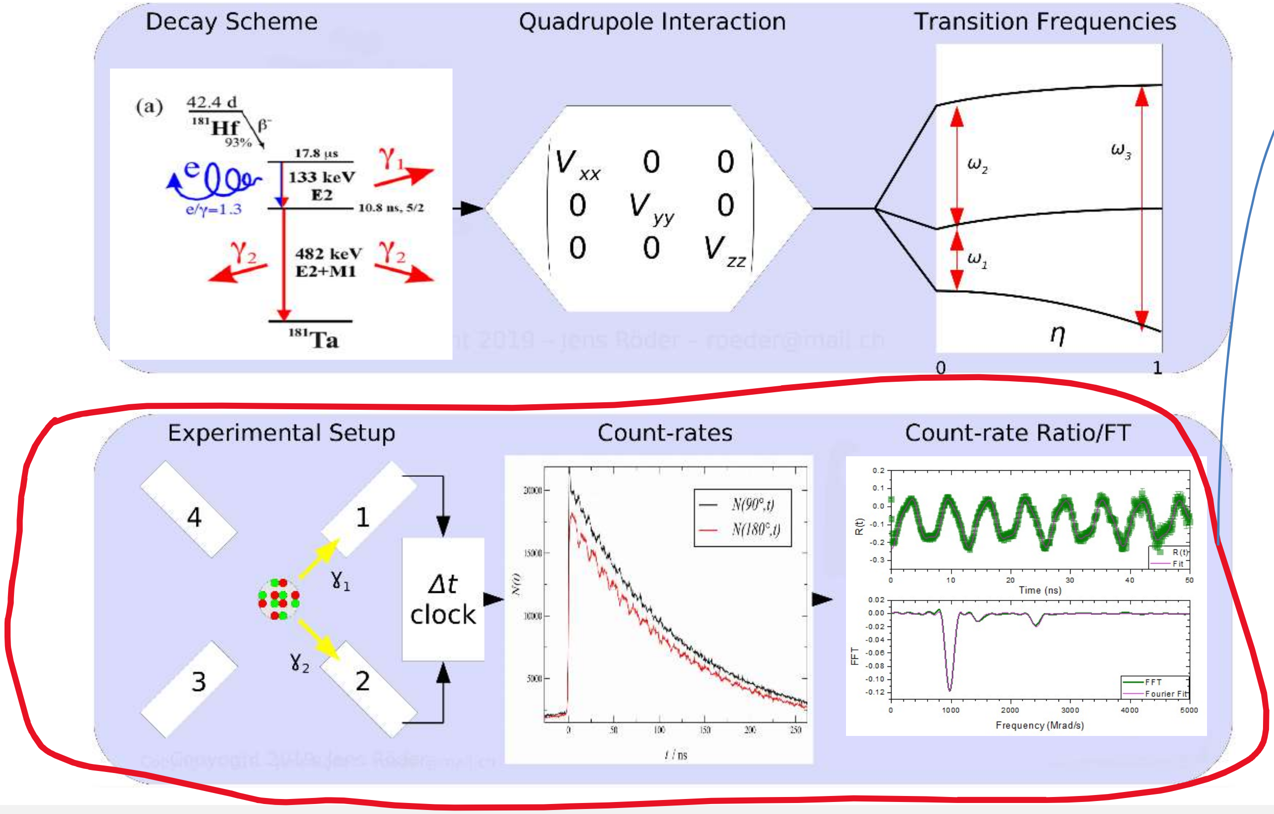
Concept of TPDAC



- **TDPAC spectroscopy:**
  - For rutile TiO_2, single crystal, we only expect significant electric quadrupole interaction.
    - Electric Field Gradients V_{ii}
      - Second Derivative of the Electric Potential.
  - For $^{181}Ta(TiO_2)$, we observe a three-fold splitting
  - Parameters: $V_{zz}, \eta = \frac{V_{yy}-V_{xx}}{V_{zz}}$
  - $|V_{zz}| > |V_{yy}| > |V_{xx}|$

Figure adapted from: Jens Röder, "Schema of PAC-Spectroscopy" – Own work, CC BY-SA 4.0, 24/11/2019, Wikipedia Entry: Perturbed angular correlation

Concept of TPDAC

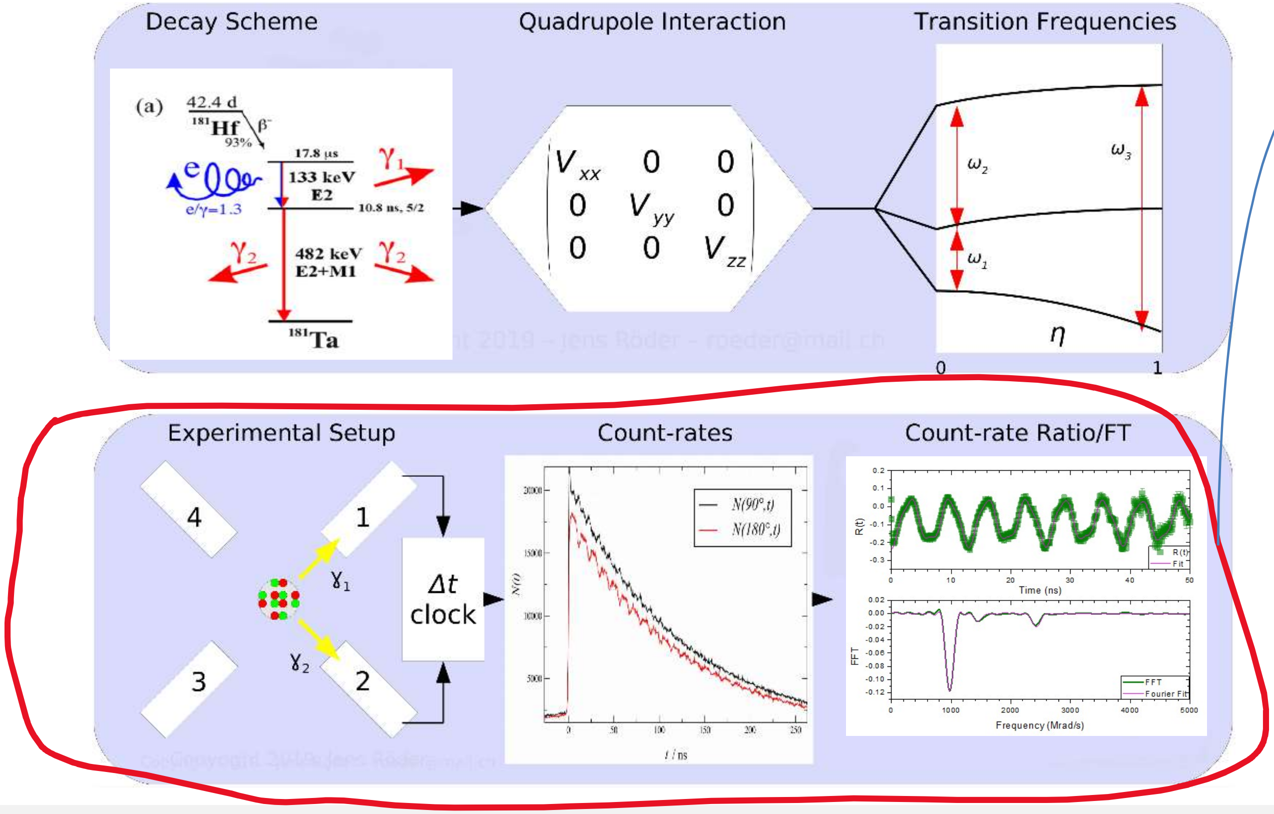


TDPAC spectroscopy:

- Our 4 detectors are arranged 90° adjacent to each other.
- Start timing: First entity detected in one detector.
- Stop timing t: Second entity detected in another detector some time later.
- $N(\theta, t) = N_0 \exp(t/t_N)\, W(\theta, t)$
  - $\theta \in \{90°, 180°\}$
  - τ_N -half life of intermediate state

Figure adapted from: Jens Röder, "Schema of PAC-Spectroscopy" – Own work, CC BY-SA 4.0, 24/11/2019, Wikipedia Entry: Perturbed angular correlation

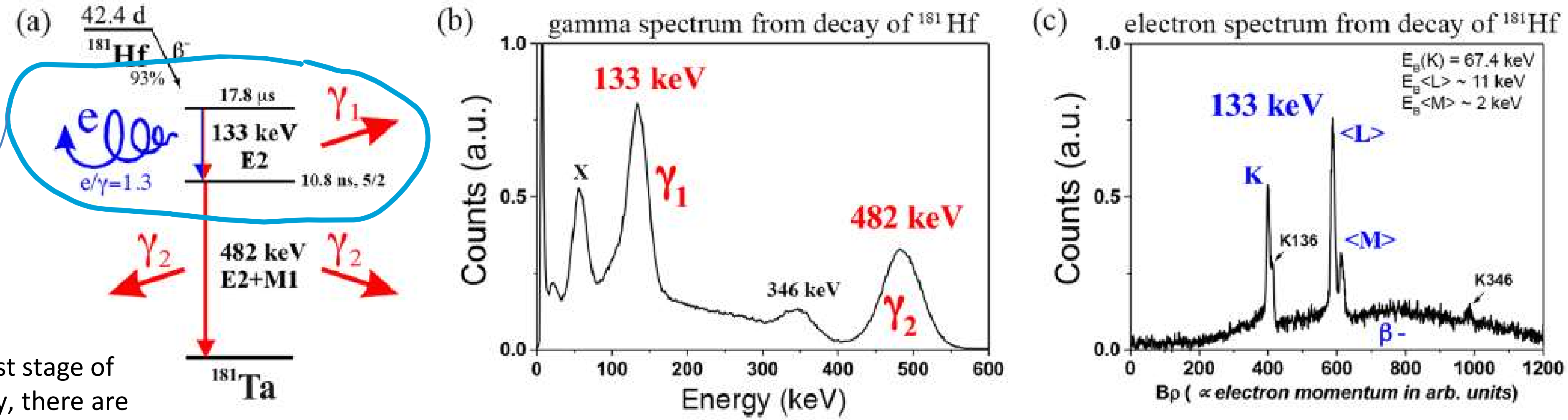
Concept of TPDAC



- **TDPAC spectroscopy:**
  - Count Rate Ratio, $R(t)$:
    - "Perturbation factor"
    - $R(t) = 2\left(\frac{N(180°,t) - N(90°,t)}{N(180°,t) + 2N(90°,t)}\right)$
  - Fitting:
    - $R(t) \approx A_{22}\left(s_0(\eta) + \sum_{i=1}^{3} s_i(\eta)\exp(-\delta\omega_i t)\cos(\omega_i t)\right)$
    - δ is the Lorentzian damping factor.

Figure adapted from: Jens Röder, "Schema of PAC-Spectroscopy" – Own work, CC BY-SA 4.0, 24/11/2019, Wikipedia Entry: Perturbed angular correlation

Concepts of TDPAC – Probe



Note:

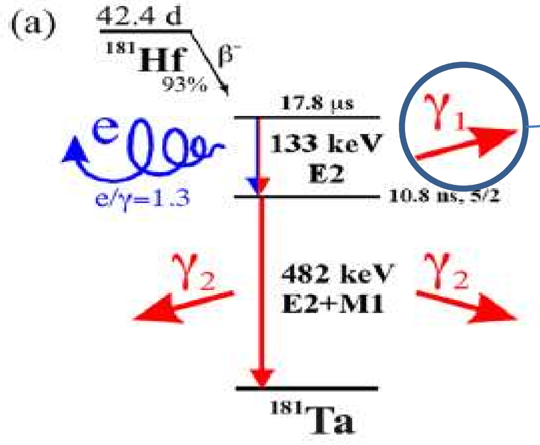
At the first stage of the Decay, there are 2 paths: Conversion electron emission/gamma emission.

Figure 1. (a) Cascade decay of ^{181}Hf/^{181}Ta and corresponding (**b**) gamma and (c) electron spectra, where the first decay of the double cascade occurs by the emission of either a photon or a conversion electron.

Figure: [Barbosa 2019]: https://doi.org/10.1038/s41598-019-52098-5

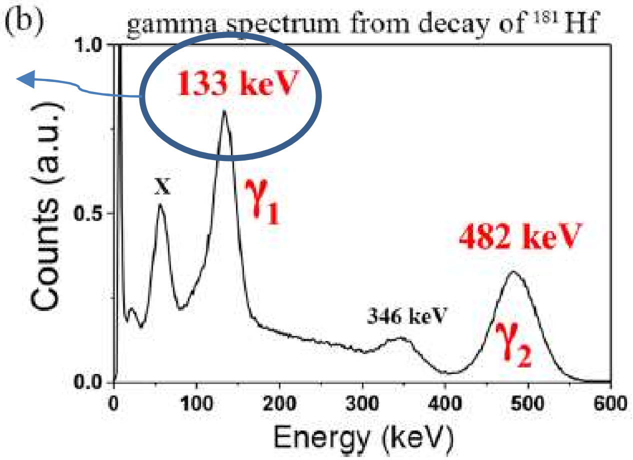
Details: [Wu 2005]: https://doi.org/10.1016/j.nds.2005.05.001

Concepts of TDPAC – Probe



$\gamma - \gamma$ TDPAC spectroscopy:

- 1st stage of decay: TDPAC probe does not interact with the electron shell of the nucleus.
- Result: Gamma emission of peak $133\ keV$

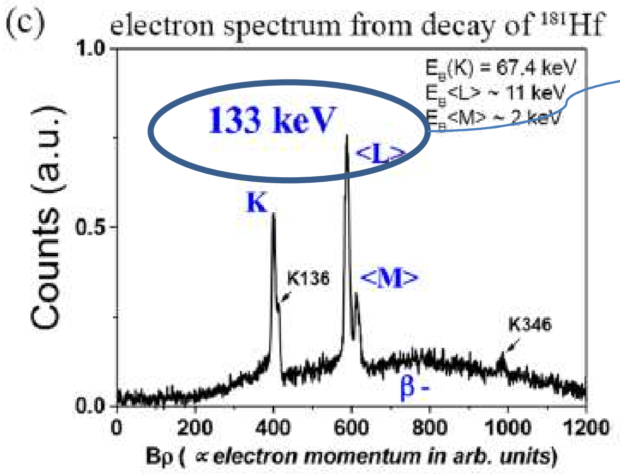


$$R(t) \approx A_{22}\left(s_0(\eta) + \sum_{i=1}^{3} s_i(\eta)\exp(-\delta\omega_i t)\cos(\omega_i t)\right)$$

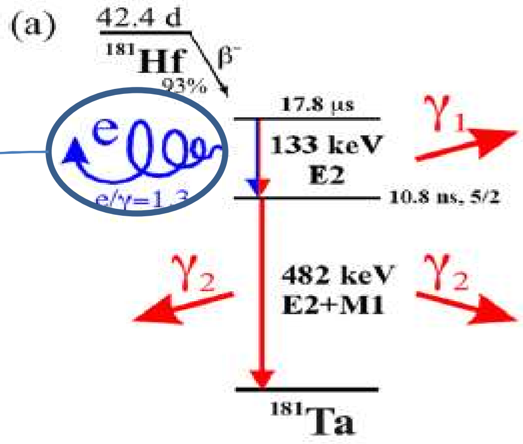
Figure: [Barbosa 2019]: https://doi.org/10.1038/s41598-019-52098-5

Concepts of TDPAC – Probe

- $e-\gamma$ **TDPAC spectroscopy:**



  - 1st stage of decay: TDPAC probe interacts with the electron shells of the nucleus.
  - Result: L-shell conversion electrons of $122\ keV\ (133\ keV - 11\ keV)$
    - [Barbosa 2019]
  - The main difference: effective $A_{kk'}$ values, which incorporates the so called b_k, the particle parameter correction factor.



$$R(t) \approx A'_{22}\left(s_0(\eta)+\sum_{i=1}^{3} s_i(\eta)\exp(-\delta\omega_i t)\cos(\omega_i t)\right);\ A'_{22}=b_2A_{22}$$

Figure: [Barbosa 2019]: https://doi.org/10.1038/s41598-019-52098-5

Concepts

- **Subtle difference between $\gamma - \gamma$ and e$-\gamma$ TDPAC**
  - Possibility of observing dynamic TDPAC signals via the recombination process.
    - If the process is in the order of ns (half life of our intermediate state) or more!

This is motivation 1:
To see if our ^{181}Ta(TiO$_2$) $e - \gamma$ parameters differ from those of $\gamma - \gamma$

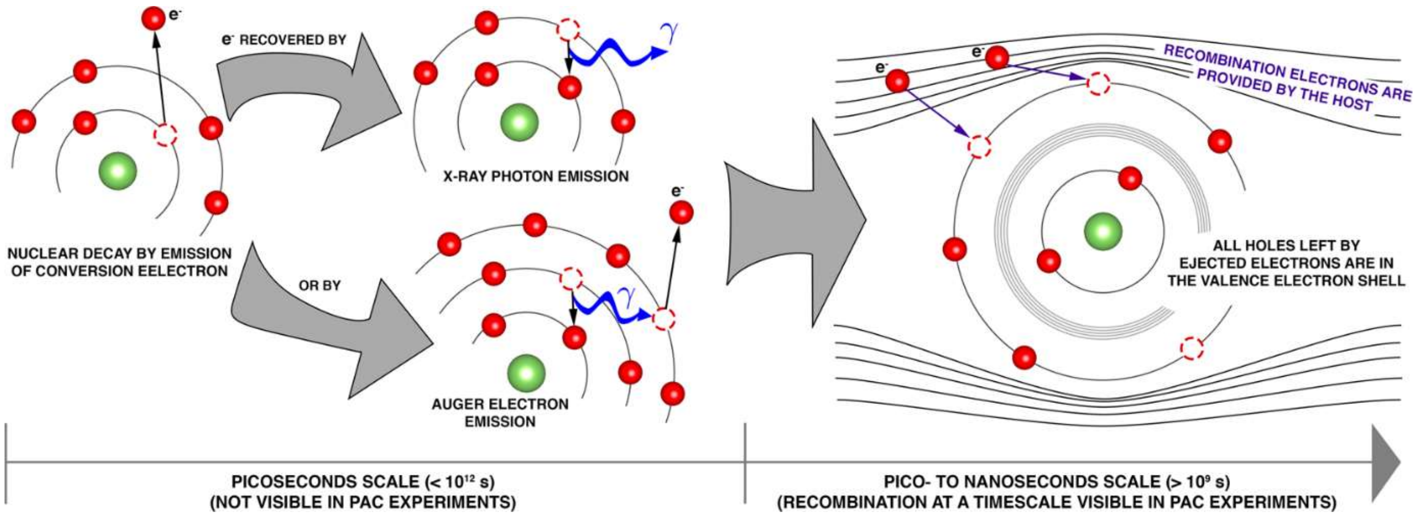
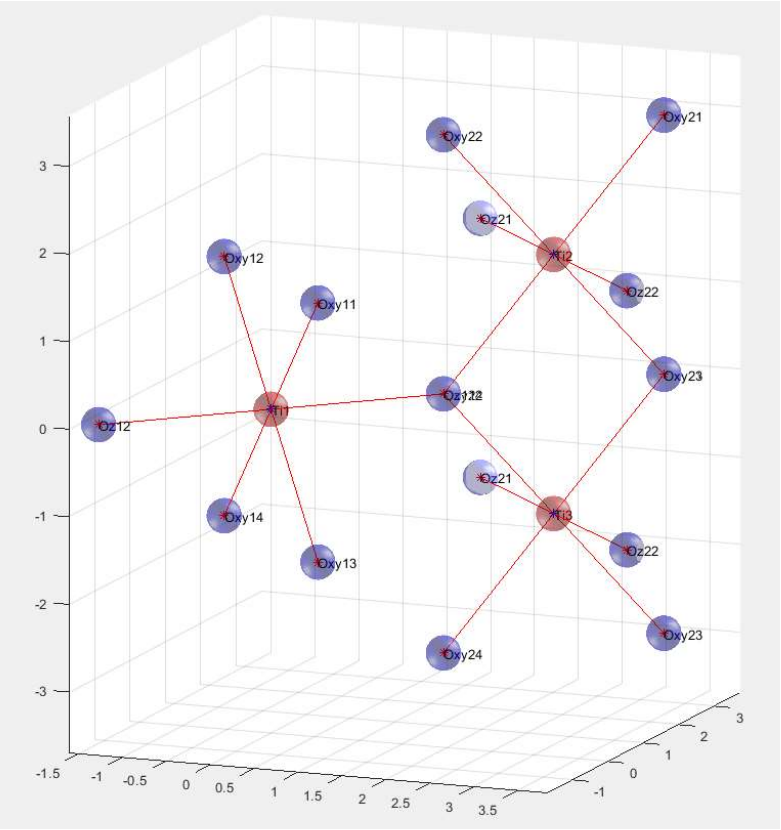


Figure: [Barbosa 2019]: https://doi.org/10.1038/s41598-019-52098-5

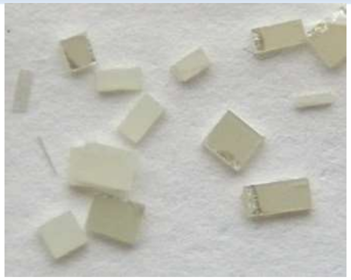
Quick overview of concepts

- **TiO_2 (rutile) crystallography:**
  - Ti^{4+} ions are 6-fold coordinated while O^{2-} atoms are 3-fold coordinated.
    - Ti^{4+} ions are surrounded by 6 O^{2-} atoms in the <u>octahedral-like configuration</u>.
- **Why TiO_2?**
  - TiO_2 has important industrial applications and is a well studied material.
  - Many hyperfine interaction studies done over a range of temperatures.
    - Suitable “Test” case!



Experimental procedures

Experimental Procedures



- **Implantation of TDPAC probe nucleus (HISKP)**
  - At the Bonn Isotope Separator, we implant ^{181}Hf isotopes (using beam sweeping) into single crystal rutile TiO_2 at the energy of 80 keV.
  - SRIM calculation predicts that ^{181}Hf isotopes are deposited with range around $28\ nm$ deep into the TiO_2 sample.
    - TDPAC will probe essentially the bulk region.
- **Important Experimental Parameters**
  - $e-\gamma$
    - A22 = -.3077, A24 = -.0494, A42 = -.0803, A44 = -.0129
  - $\gamma-\gamma$
    - A22 = -.2213, A24 = -.0276, A42 = -.1491, A44 = -.0186

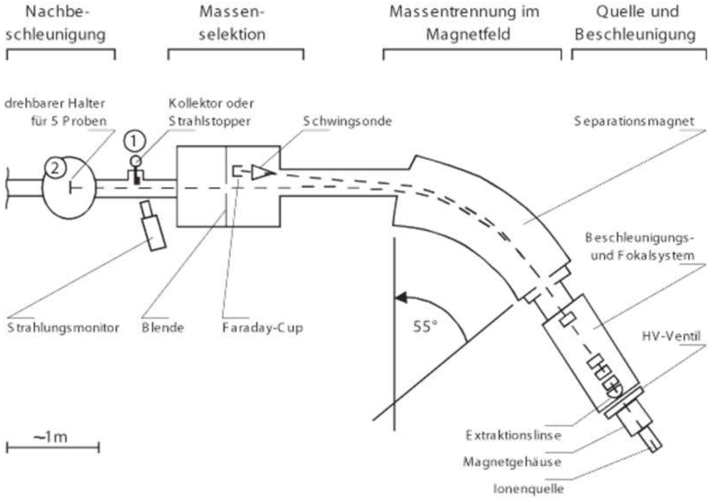
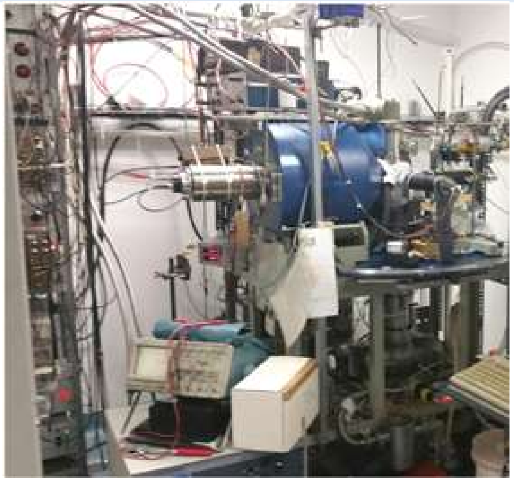


Figure taken from: https://tdpac.hiskp.uni-bonn.de/pac/

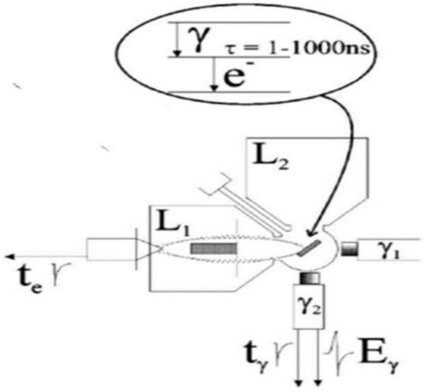
Experimental Procedures



Important Experimental Parameters:

- Annealing time:
  - 5 hours and 15 minutes in oven of $873.15\ K$ in vacuum.
- Quadrupole moment of ^{181}Ta:
  - $2.36 \pm 0.05\ barns$
    - [Butz 1983]: https://doi.org/10.1016/0375-9601(83)90362-6
- Temperature range:
  - $\gamma - \gamma$: Room temperature.
  - $e - \gamma$: $39.3\ K$ to $474.15\ K$, in both cryostat and furnace.
- More information on the ISOLDE $e - \gamma$ TDPAC machine/estimation of Akk:

[Marques 1994]: $e - \gamma$ setup in ISOLDE: https://doi.org/10.1016/0168-583X(94)00591-5
[Kleinheinz 1965]: Physics of electron detectors: https://doi.org/10.1016/0029-554X(65)90466-0
[Correia 2020]: Private communication with J.G. Correia-See details at the end of this presentation document.

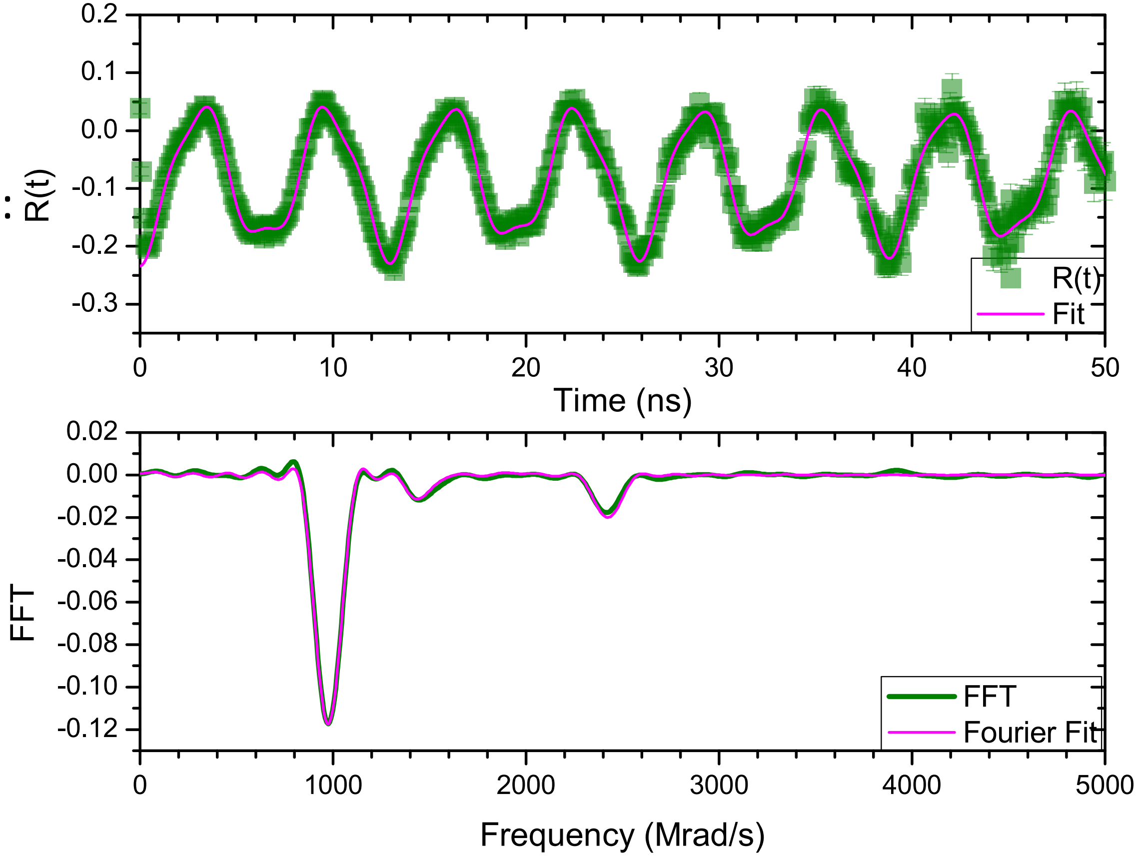


Adopted from [Karl 2017]. https://doi.org/10.1088/1361-6471/aa81ac

Results for Room Temperature

Results for Room Temperature:

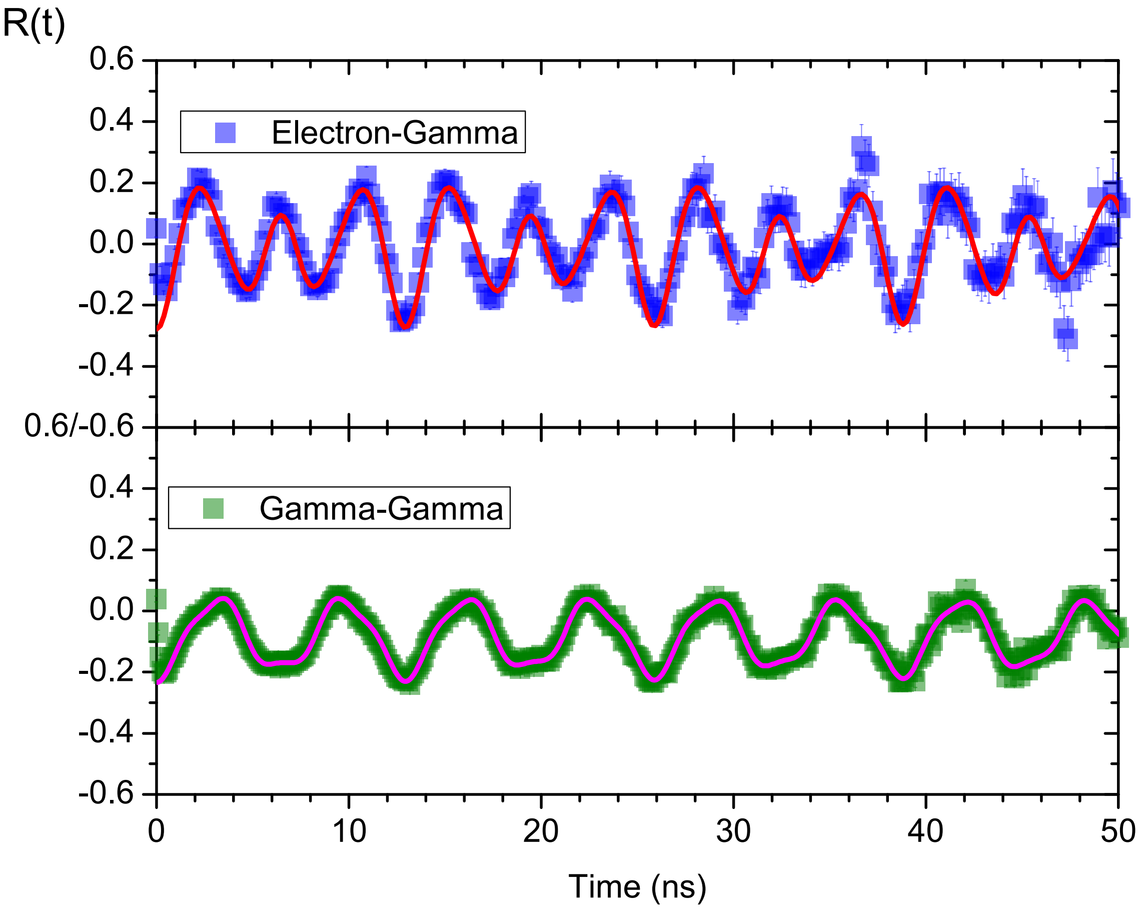
- $\gamma - \gamma\ \boldsymbol{TDPAC}$:
  - <u>Single measurement</u> at Room Temperature:
    - $\omega_0 = 762 \pm 0.1\ Mrad/s$
    - $\eta : 0.542 \pm 0.001$
    - $\delta : 0.17 \pm 0.03\ \%$
    - $V_{zz} : 142 \pm 3\ (10^{20}\ Vm^{-2})$.



$R(t)$ is the TDPAC observable in which all the information of hyperfine parameters is contained and extracted.

Results for RT:

- $e - \gamma$ ***TDPAC*:**
  - Room Temperature Results:
    - Sample population: 12
    - $\omega_0 = 764.7 \pm 0.5\ Mrad/s$
    - $\eta : 0.544 \pm 0.005$
    - $\delta : 0.05 \pm 0.03\ \%$
    - $V_{zz} : 142 \pm 3\ (10^{20}\ Vm^{-2})$
- $\gamma - \gamma$ ***TDPAC*:**
  - Single measurement at Room Temperature:
    - $\omega_0 = 762 \pm 0.1\ Mrad/s$
    - $\eta : 0.542 \pm 0.001$
    - $\delta : 0.17 \pm 0.03\ \%$
    - $V_{zz} : 142 \pm 3\ (10^{20}\ Vm^{-2})$.



Comparison with Literature (RT):

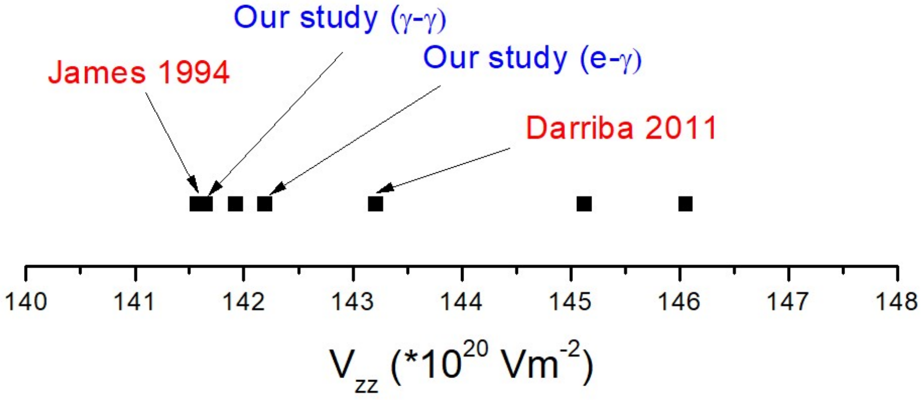
Paper	V_{zz} (10^{20} Vm^{-2})	Asymmetry Parameter	Delta Lorentzian (%)	Crystal Type	Sample Preparation
James 1994	141.57	0.57	0.01	Polycrystal	Thermal Annealing at 1570K for several hrs
Darriba 2011	143.20	0.555	0.4	Single Crystal	Thermal Annealing at 873K for 6hr
Banerjee 2016	141.92	0.56	0.6	Polycrystal	Thermal Annealing at 1273K for 10hr
Satyendra 2009	145.12	0.56	Unknown	Polycrystal	Thermal Annealing at 1273K for 10hr
Banerjee 2010 {S4}	149.51	0.51	5.2	Polycrystal	Thermal Annealing at 1123K for 4hr
Banerjee 2010 {S7}	146.05	0.51	1	Polycrystal	Thermal Annealing Anatase TiO2 at 1223K for 8hr (Convert to Rutile TiO2)
This study ($\gamma - \gamma$)	141.64	0.542	0.17	Single Crystal	Thermal Annealing at 873K for 5hr
This study ($e - \gamma$)	142.19	0.544	0.05	Single Crystal	Thermal Annealing at 873K for 5hr

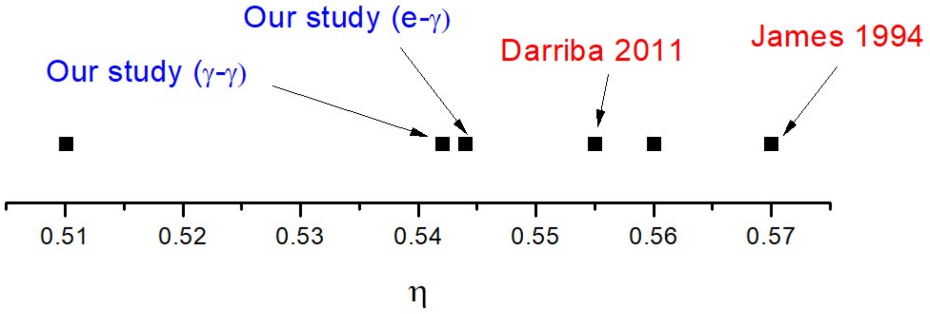
We have a Low delta (attenuation), corresponding to sharp peaks.
The three frequencies are relatively well defined.

Our experimental asymmetry parameter agrees with the quoted values up to 0.05.

Our V_{zz} (and ω_0 in extension) follow established values up to the order of magnitude.

Comparison with Literature (RT):





Our experimental asymmetry parameter agrees with the quoted values up to 0.05.

Our V_{zz} (and ω_0 in extension) follow established values up to the order of magnitude.

Comments and Analysis:

- ***Comments on the room temperature TDPAC results***:
  - Our hyperfine parameters for $\gamma - \gamma$ & $e - \gamma$ TDPAC are in good agreement with the literature.
    - The electronic recombination (electron cascade) following the internal conversion of the L shell electron is of a time scale much lesser (ps) than the intermediate lifetime ($10.8ns$) of the metastable ^{181}Ta state.

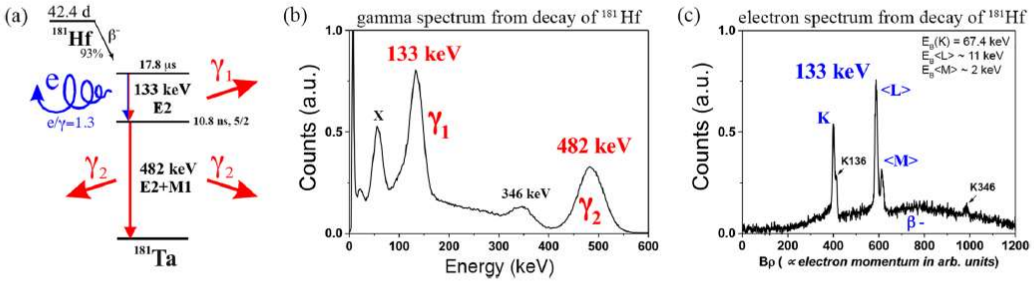
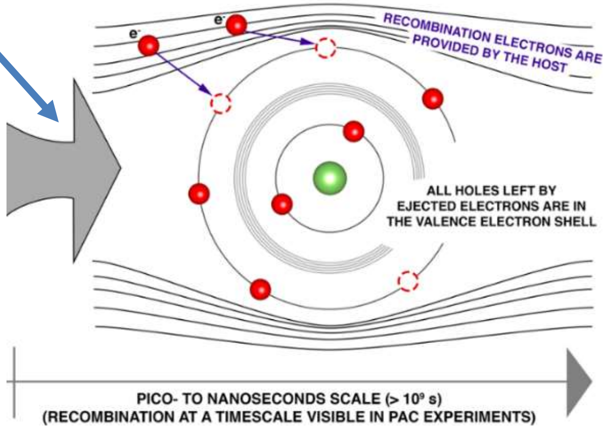


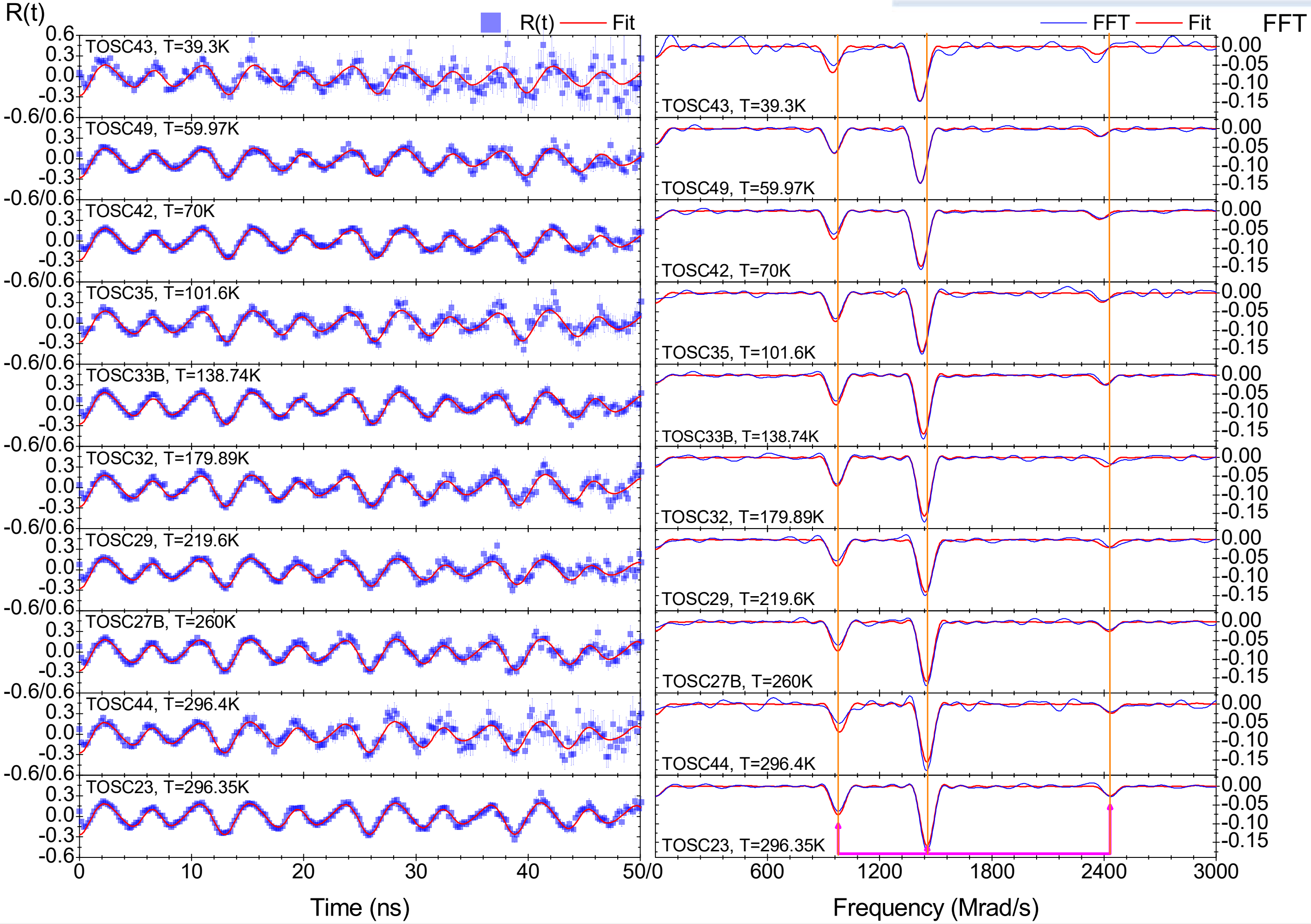
Figure 1. (a) Cascade decay of ^{181}Hf/^{181}Ta and corresponding (**b**) gamma and (**c**) electron spectra, where the first decay of the double cascade occurs by the emission of either a photon or a conversion electron.

Figure: [Barbosa 2019]: https://doi.org/10.1038/s41598-019-52098-5

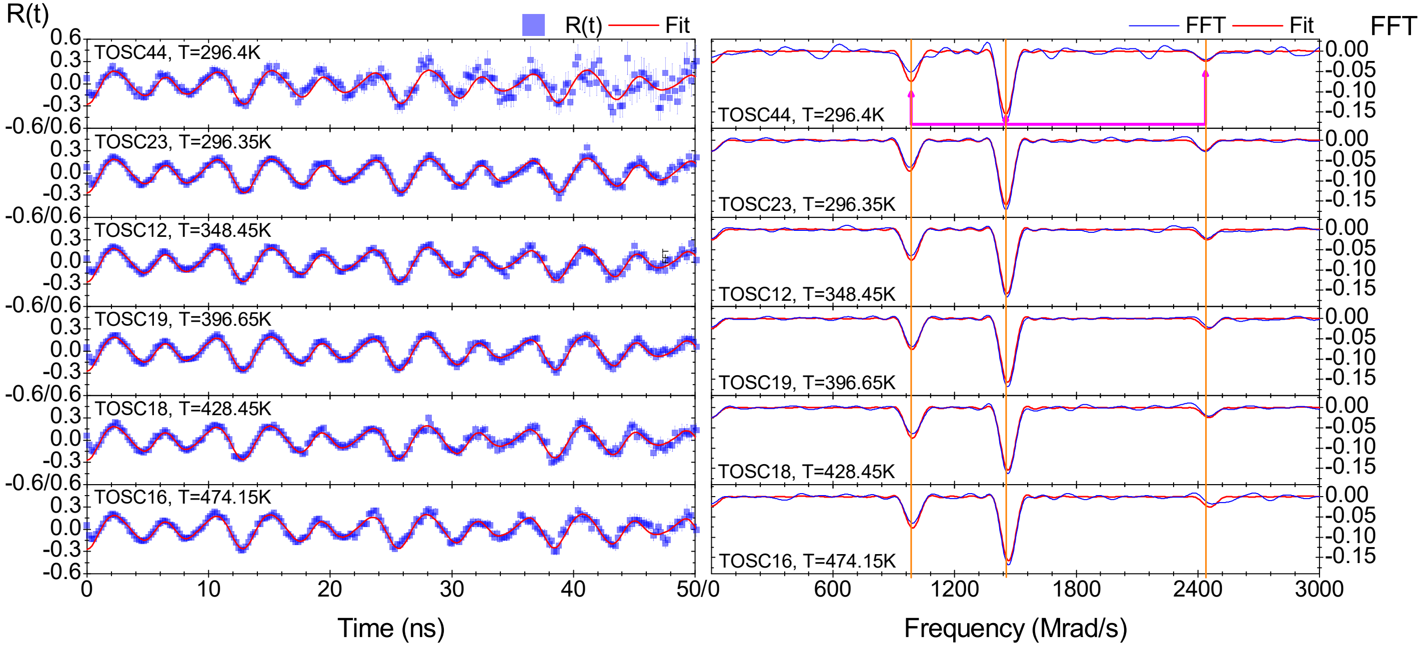


Temperature measurements from 39 K to 474 K

$e - \gamma$ TDPAC Spectra:

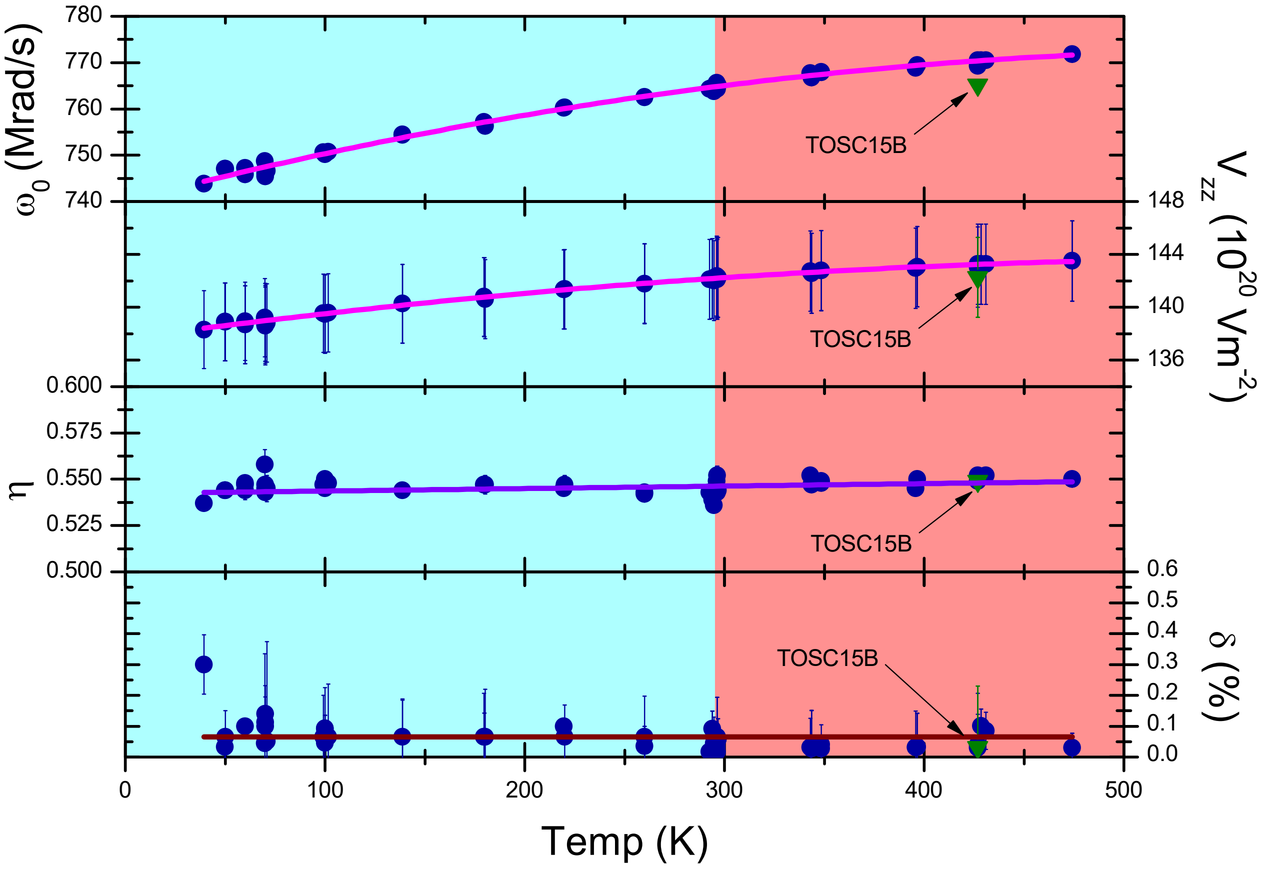


$e - \gamma$ TDPAC Spectra:

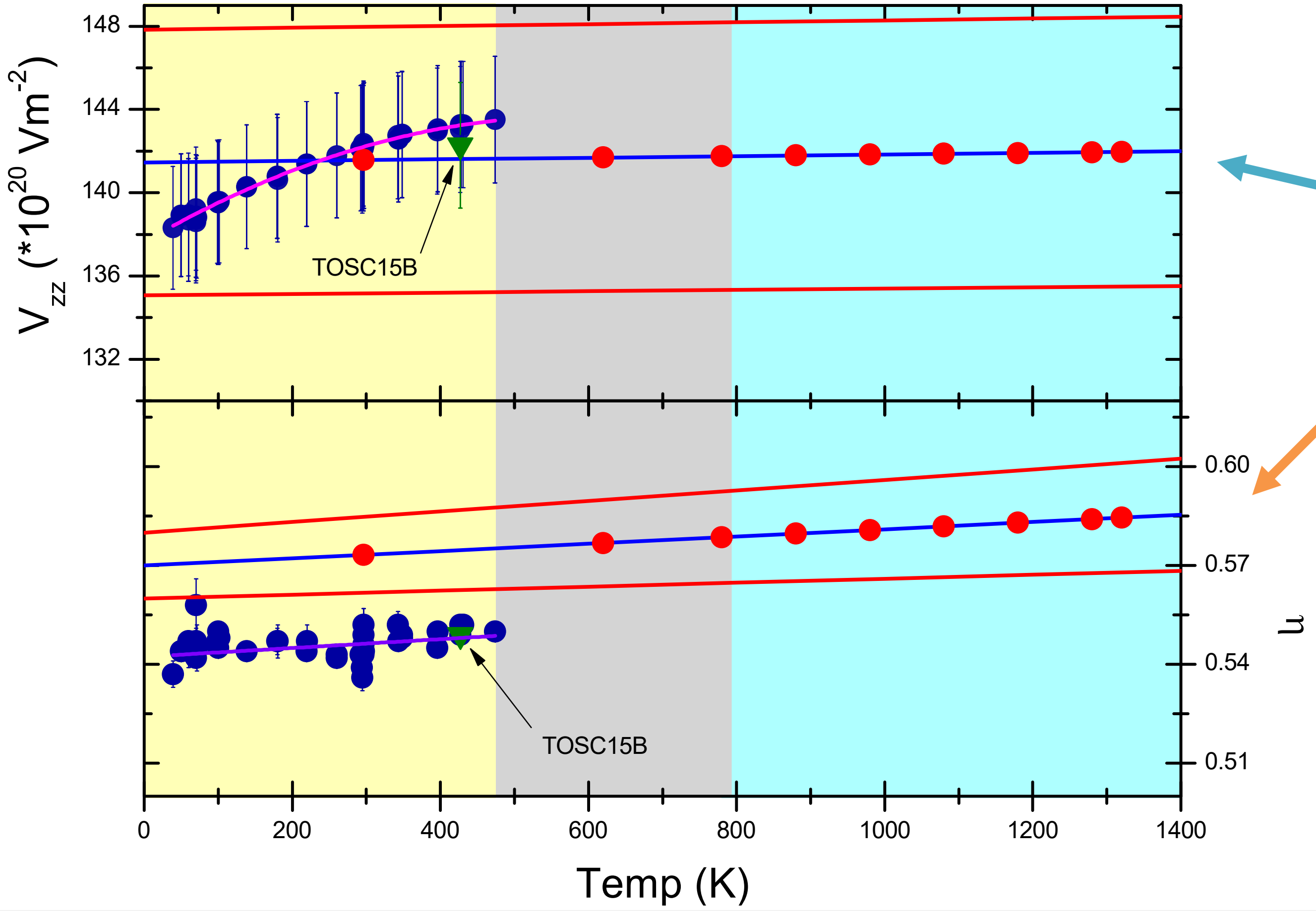


Selected TDPAC spectra arranged in order of increasing temperature.
Qualitatively, note the systematic shift in the peaks, especially on the rightmost peak (increasing shift)

$e-\gamma$ Graphs of hyperfine parameters:



- The equation of fit for ω_0 is
  - $740.1(3) + 0.112(3) * T - 0.000096(5) * T^2 \ Mrad/s$
- The equation of fit for V_{zz} is
  - $137.63(6) + 0.0207(5) * T - 0.000017(1) * T^2 \ (10^{20} \ Vm^{-2})$



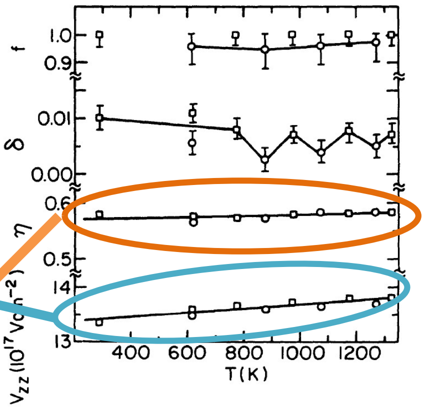
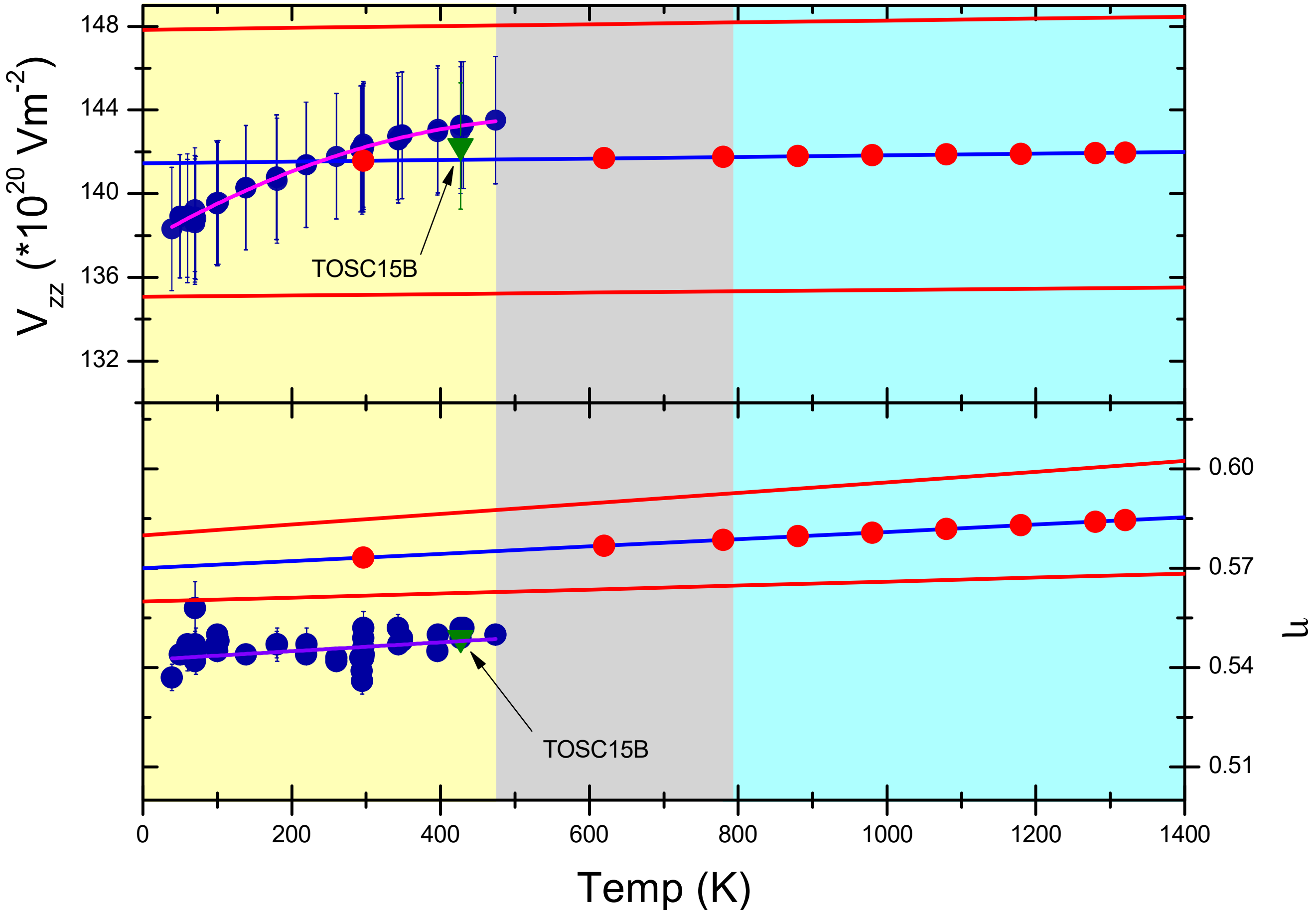


FIG. 4. Temperature dependence of the electric-field-gradient parameters for several samples of TiO_2 doped with the $^{181}Hf \rightarrow ^{181}Ta$ probe. When error bars are not shown, the uncertainties do not exceed the size of the data points. The solid lines through the V_{zz} and η data points represent least-squares fits, which give slopes and intercepts of $3.6\pm0.6\times10^{12}$ V cm^{-2} K^{-1} and $13.30\pm0.06\times10^{17}$ V cm^{-2} for V_{zz} and $1.1\pm0.5\times10^{-5}$ K^{-1} and 0.57 ± 0.01 for η.

Quick notes:
Concave polynomial trend in the yellow region
Increasing linear trend in the blue region
No recorded experimental trend at the grey region

[James 1994]: https://doi.org/10.1103/physrevb.50.1264



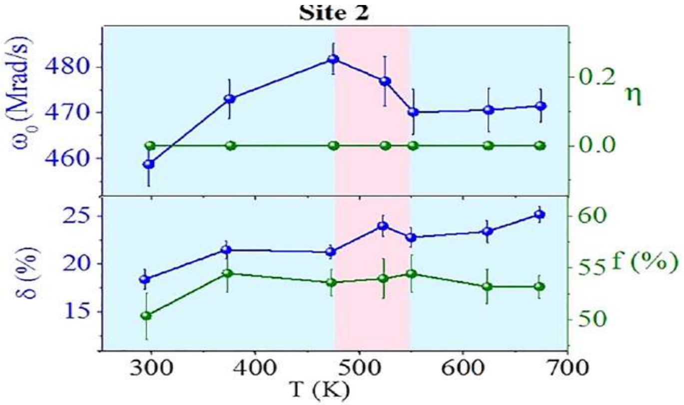
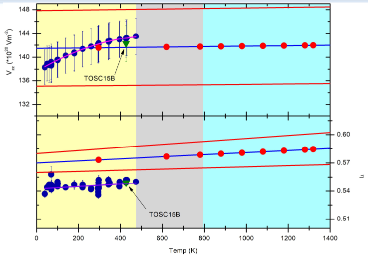


FIG. 4. Hyperfine parameters and their respective errors in the TiO$_2$ thin film using ^{181}Hf(^{181}Ta) as the test nucleus. Some error bars cannot be seen, because their uncertainties are smaller than the data points.

[Schell 2017] https://doi.org/10.1063/1.4980168



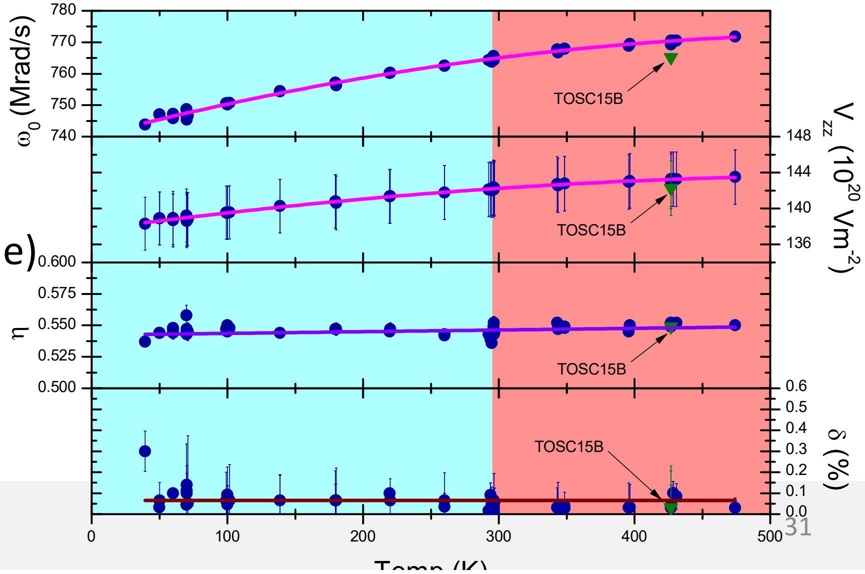
Comments and Analysis:

- **Comments on the $e-\gamma$ $TDPAC$ with varying temperature:**
  - Contrary to the conjecture from [James 1994], [Darriba 2011], we have a non-linear increase in V_{zz} at the low temperature region.
  - Results from [Schell 2017] shows a similar trend with anatase ^{181}Ta(TiO_2) thin film.
    - It is highly likely that there is a significant physics behind this observed trend.
    - Origin(?): Lattice expansion/phonon modes, lattice relaxation around impurity ion, localized electron orbitals, possible thermal repopulation of electron states [Butz 2012]
    - We are currently exploring on the frozen phonon modes using the CP-PAW program developed by Prof Peter Bloechl, with his involvement as a theoretical physicist.
  - Trend from [Schell 2017], [James 1994] and [Darriba 2011] suggest for our result: A parabolic decrease in the region $\sim 475\ K$ to $\sim 800\ K$, with a local maxima at the temperature of around $500\ K$.

[Schell 2017]: https://doi.org/10.1063/1.4980168
[Butz 2012]: https://doi.org/10.1007/s10751-012-0675-7

Key takeaways, project status and acknowledgements:

- Key-pointers:
  - For ^{181}Ta(TiO$_2$), we cannot detect the difference between the spectra of the $e-\gamma$ and $\gamma-\gamma$ TDPAC.
    - This is because electron recombination is (at least) in the order of ps, compared to the lifetime of the intermediate state (ns).
  - We detect a surprising parabolic trend of V_{zz} and ω_0 at the low temperature region.
  - We are currently doing a CP-PAW DFT simulation of ^{181}Ta(TiO$_2$)
    - Frozen Phonon Mode EFG calculation of pure TiO$_2$ first: RESULTS SOON!
- Acknowledgements:
  - Source of funding for implantation equipment: BMBF
    - Grants 05K13MG1 and 05K16PGA.
  - License for CP-PAW:
    - Peter Bloechl (End user license granted to Ian Yap Chang Jie)
  - Gfit19 and Interlude assistance, alongside data-taking:
    - J.G.Correia
  - And to my awesome papa and mama:
    - Who provided me a Threadripper 3970x for CP-PAW.



BACKUP SLIDES:

Extra slides

For questions that involves the $e-\gamma$ detector and the decay path of the ^{181}Ta(TiO_2)

Concept of TPDAC

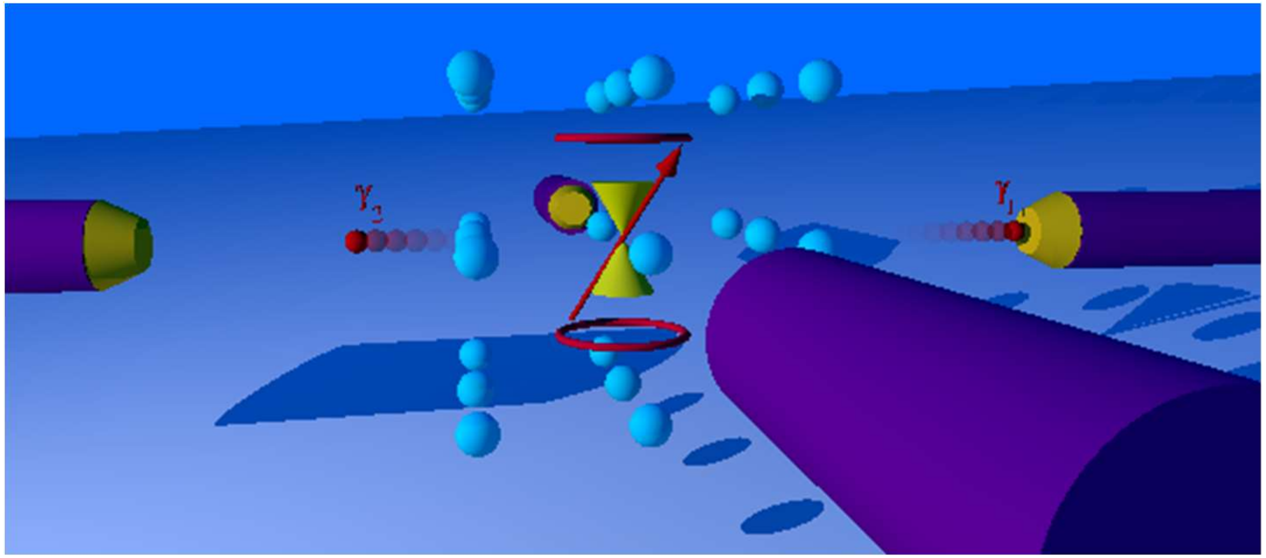


Figure adapted from: Jens Röder, “Nuclear probe in a lattice” –Own work, CC BY-SA 4.0, 10/11/2019, Wikipedia Entry: Perturbed angular correlation

- **TDPAC spectroscopy:**
  - Signal is acquired from consecutive emission of two correlated entities from decay of TDPAC probe.
    - Specifically, their “*angular*” direction of emissions.
  - Nucleus is subjected to hyperfine interaction: Magnetic dipole, Electric quadrupole, or combined, from the local environment of the lattice site.

Advantages of TDPAC

- **Sensitive:**
  - Parts of billions of TDPAC probe nucleus only needed for effective characterization.
- **Local:**
  - TDPAC probe nucleus senses only its immediate surroundings.
    - Ability to detect different sites (Subject to annealing and implantation conditions) and type of host materials.
- **Robust:**
  - TDPAC spectroscopy can be conducted over a wide range of temperatures and conditions (Solid/Liquid).

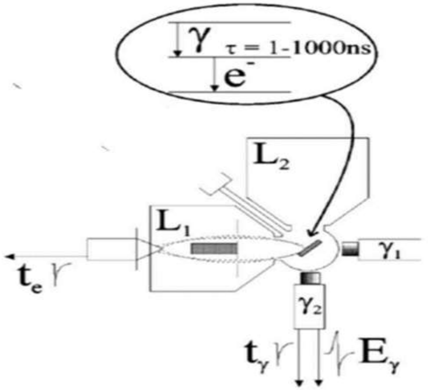
$e-\gamma$ TPDAC spectrometer in ISOLDE:

- Overview:
  - We are the only group in the world to have a working $e-\gamma$ TDPAC spectrometer for the acquisition of data with varying probes and materials.
    - It is used extensively in HISKP, University of Bonn from the 1970's, before being upgraded and installed in ISOLDE, CERN.
  - Augmented with $\gamma-\gamma$ TDPAC spectroscopy, we can use a wider range of probes to study materials in an exotic way.
    - Higher conversion (thus detection rate)
    - Larger anisotropy
    - Favorable particle parameter, etc
  - Possibilities of different $R(t)$ signals corresponding to the different physics behind $e-\gamma$ and $\gamma-\gamma$ spectroscopy.

$e-\gamma$ TPDAC spectrometer in ISOLDE:

- Experimental Setup:
  - The $e-\gamma$ spectrometer is made up of 4 detectors:
    - Two magnetic lenses of Siegbahn type [Kleinheinz 1965] for electron detection
      - Better energy resolution of detection than BaF_2 scintillators
    - Two BaF_2 scintillators for γ detection.
      - For reference, we use scintillator detectors of type $LaBr_3$ for $\gamma-\gamma$ TDPAC
    - Arranged in a 90° planar setup.
  - $R(t)=\frac{2\left(N(180°,t)-N(90°,t)\right)}{N(180°,t)+2N(90°,t)}\approx b_2A_{22}G_{22}(t)$ (Polycrystalline)
    - b_2 is the particle parameter.

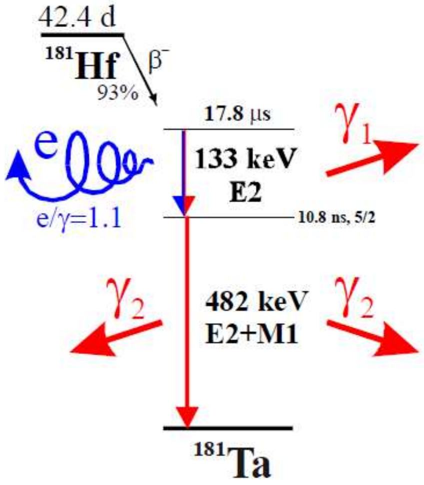
[Marques 1994], $e-\gamma$ setup in ISOLDE: https://doi.org/10.1016/0168-583X(94)00591-5
[Kleinheinz 1965], physics of electron detectors: https://doi.org/10.1016/0029-554X(65)90466-0



Adopted from [Karl 2017]. https://doi.org/10.1088/1361-6471/aa81ac

Decay scheme of ^{181}Hf → ^{181}Ta :

- Decay process:
  - ^{181}Hf undergoes a β^- decay to an excited ^{181}Ta state which then undergoes a two-stage consecutive deexcitation to ground state ^{181}Ta.
  - Stage 1:
    - Excited ^{181}Ta state undergoes either an internal conversion process or a de-excitation process, producing an electron or a gamma photon, respectively.
    - Note that the half-life of the metastable ^{181}Ta state is $10.8\ ns$.
    - Also note that the ratio of the formation of electron to gamma photon is 1.1.
  - Stage 2:
    - Metastable ^{181}Ta state undergoes a second de-excitation process.
      - This produce the secondary gamma photon.



Details are found in [Wu 2005]. https://doi.org/10.1016/j.nds.2005.05.001
Figure adapted from J.G Correia in a private communication.

DETAILS OF PRIVATE COMMUNICATION:

Details of Private Communication

With J.G.Correia

Details for γ Akk coefficents:

- [JG02]: Private communication with J.G. Correia
- Obtained with program multiAkk (J.G. Correia and J.G. Marques) that generates angular correlation coefficients (bk)Akk'(bk')
- For multiple gamma - gamma and electron-gamma nuclear cascades based on refs: R. S. HAGER and E. C. SELTZER, NUCLEAR DATA A4, 397-641 (1968) https://doi.org/10.1216/S0550-306X(68)80017-5 and R. S. HAGER and E. C. SELTZER, NUCLEAR DATA A4, 1-235 (1968) https://doi.org/10.1216/S0550-306X(68)80002-3
- The program further includes gamma finite size (gamma) attenuations coefficients Qkk' which were analytical calculated based on ref. M.E.Rose "The Analysis of Angular Correlation and Angular Distribution Data" Physical Review 91, 610, (1953) https://doi.org/10.1103/PhysRev.91.610

Details for electron attenuation coefficients:

- [JG03]: Private communication with J.G.Correia
- Qk(e-) anisotropy attenuation coefficients consider electron (back)scattering on sample and spectrometer geometry acceptance solid angle determined with the esP2P4 program that was built on purpose and integrates modified versions of Penelope and penEasy programs, ref.
- J. Baró, J. Sempau, J.M. Fernández-Varea and F. Salvat "PENELOPE: an algorithm for Monte Carlo simulation of the penetration and energy loss of electrons and positrons in matter" Nucl. Instrum. Meth. B 100 (1995) 31–46. https://doi.org/10.1016/0168-583X(95)00349-5.

Data treatment and Fitting

Data treatment and Fitting

- Data Analysis:
  - $R(t)$, the TDPAC observable anisotropy ratio is built from raw coincidence spectra with PRELUDE.
  - We then use Gfit19 (Modified version of Nnfit program) to fit $R(t)$:
    - From literature, we do expect only significant electric quadrupole interaction.
    - 3 peaks in the FFT spectra, since $I = 5/2$ for ^{181}Ta
  - We then plot out the relevant parameters with respect to temperature:
    - Largest component of the electric field gradient, V_{zz}
    - Fundamental frequency ω_0
    - Asymmetry parameter η
    - Delta Lorentzian (Damping) δ
    - Single crystal orientation of ^{181}Ta(TiO_2) with respect to the geometry of the detectors φ, θ.

Introduction (Theoretical)

Introduction (Theoretical) and project status:

- **Research Investigation:**
  - We are going to do a first principles calculation onto ^{181}Ta(TiO_2) with varying temperature from $0\ K\ to\ 1200\ K$.
  - From user preference, we use a specific Density Functional Technique (DFT), called the Car-Parrinello Projected Augmented Wave (CP-PAW) method developed by Prof Peter Blöchl.
- **Why?**
  - TPDAC studies of ^{181}Ta(TiO_2) reveals a surprisingly a non-linear relation between the largest electric field gradient and temperature and is suspected to be parabolic in nature. The asymmetry parameter does not change much though.
    - This poses several theoretical questions:
      - Which factors contribute to the parabolic relationship as seen in our result earlier?
      - With respect to temperature, how does the octahedral structure (^{181}Ta as central ion surrounded by 6 oxygen atoms) in the ^{181}Ta(TiO_2) sample stretch or deform?
      - Does phonons play a part? Does harmonic effects provide a sufficient explanation, or anharmonic effects needs to be included as well?

Introduction (Theoretical) and project status:

Current Status:

- We are almost able to get a self consistent 2 by 2 by 3 (TiO_2) supercell with ^{181}Ta replacing one Ti at $0\ K$.
    - Technical issues still needs to be resolved.
- We will then execute the frozen phonon calculation, where we restrict the movement of Ta displacement towards one of the neighbours.