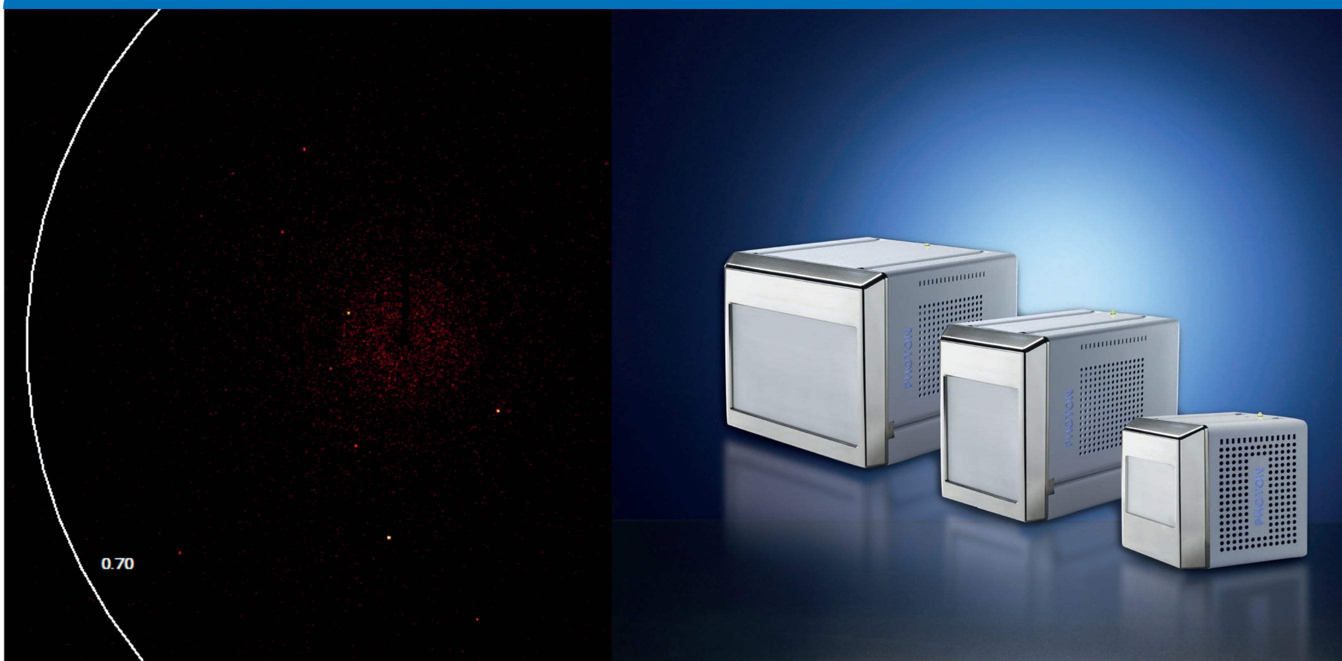


Application Note SC-XRD 527

The New PHOTON III Detector with Photon Counting in Mixed-Mode Detection

- A PHOTON II versus PHOTON III comparison

Introduction

CCD detectors for Single Crystal X-ray Diffraction (SC-XRD) were commercially introduced in 1994, with the APEX II detector deemed as the culmination of the technology well into the 2000s. Even today, many sites around the world are still collecting quality data using diffraction systems that prominently feature the APEX II detector.

Today's state-of-the art detectors are charge-integrating pixel array detectors (CPADs) that were developed for 4th generation XFEL synchrotron beam lines. To cope with extraordinarily high X-ray dose, XFEL detectors are typically operated in charge-integration mode with a high read out frequency. At the end of 2015, Bruker introduced the PHOTON II, a CPAD X-ray detector that follows the very same design concept adapted to the needs of in-house crystallography.

Figure 1: D8 VENTURE and D8 QUEST with PHOTON detector and METALJET (left) and IμS 3.0 source (right).

In addition to the characteristics mentioned above, XFEL detectors, such as the JUNGFRAU detector, developed for SWISSFEL, feature Mixed-Mode detection. Mixed-Mode operation adds single photon counting capability to traditional charge-integration. This feature introduces detectors, which in contrast to Hybrid Pixel Counters (HPCs) and Hybrid Pixel Area Detectors (HPADs) do not suffer from charge-sharing noise and pulse pile up. While the HPCs perform photon counting in the time domain, Mixed-Mode HPAD detectors operate in the space domain. Space domain operation ensures that no photons are lost even with high X-ray dose. This feature became available to the in-house market in 2017 with the launch of the PHOTON III Mixed-Mode detectors. (Figure 2). The PHOTON III also suppresses high-energy events ('Zingers' caused for example by cosmic rays) using High Energy Event Discrimination (HEED).

Comparing the PHOTON II to the PHOTON III

The PHOTON II is operated in the traditional charge-integration mode with highest dynamic range and minimum background noise.

The advanced PHOTON III technology additionally allows to operate the detector in two modes: traditional charge-integration mode and the newly developed Mixed-Mode; providing single photon-counting with highest accuracy.

The PHOTON II offers the unique capability to read the charge in a pixel multiple times without destroying or disturbing the charge (Non-Destructive Readout, NDR). By repeatedly measuring the pixel charge, the PHOTON II improves data precision and accuracy. Combined with the patented Adaptive Oversampling (AO) —

which is matching detector operation to the diffraction properties of the sample — this results in an extended dynamic range far beyond the factor of two, which is possible with simple double-sampling used at CCD times. This method of operation provides high-quality data sets with high dynamic range and very low noise, even for relatively long exposure times.

In addition, the PHOTON III detector can also integrate charges from the X-ray signal in the space domain: sub-frames are read with a frequency of 70 Hz without deadtime. A high performance Field Programmable Gate Array pipeline analyzes the sub-frame data in real time by comparing subsequent frames, which identifies all single photon events. This guarantees single-photon sensitivity and data quality even for the most weakly diffracting samples (Figure 3). From a hardware point of view, the PHOTON III requires a significantly more powerful data processing unit, compared to the PHOTON II. The approach of processing raw detector data on the sub-frame level in the space domain enables the PHOTON III detector to overcome drawbacks intrinsic to direct counting HPC/HPAD detectors. Operating in time domain, these detectors are prone to suffering from severe errors like pulse pileup, charge sharing and parallax. Furthermore, HPC/HPAD detectors show limited sensitivity for hard radiation — such as Mo Kα or Ag Kα — when Silicon (Si) is used to absorb the X-ray photons.

Figure 2: PHOTON III 28, PHOTON III 14, and PHOTON III 7: Photon-counting Mixed-Mode detector family.

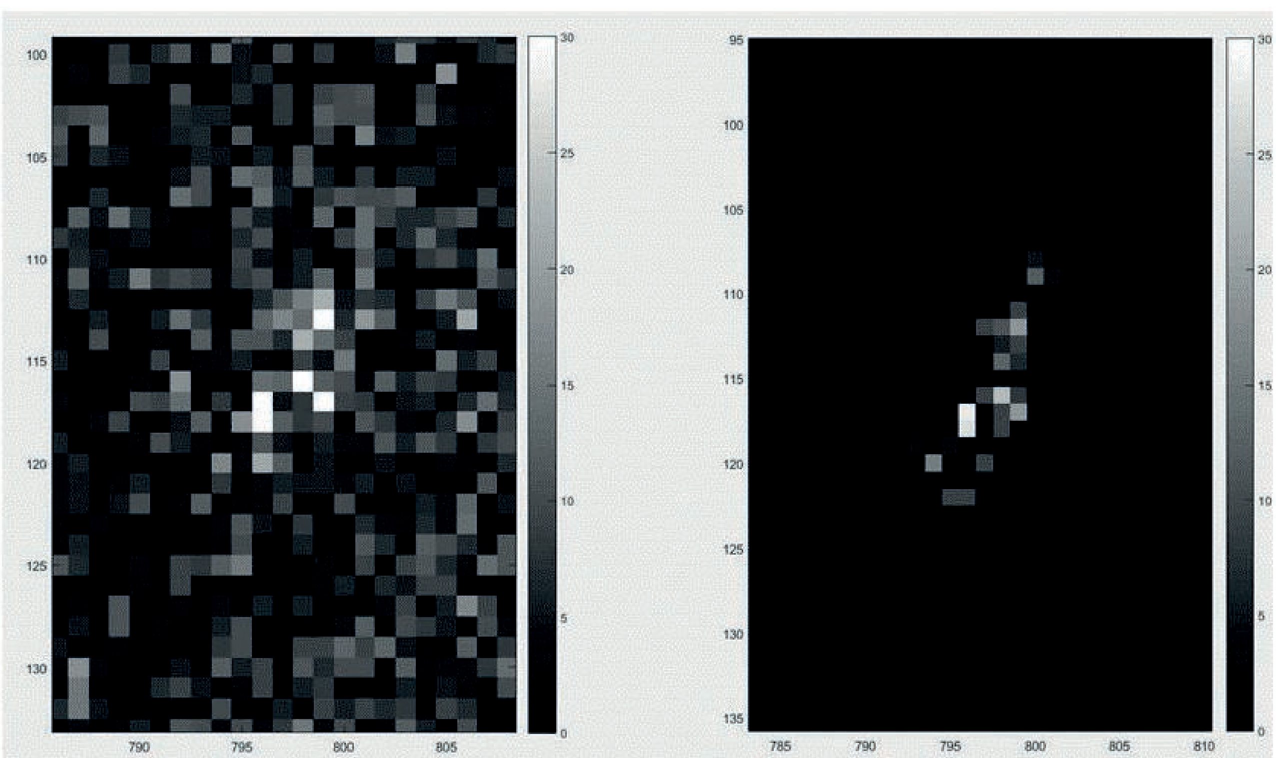


Figure 3: In a 5 minute exposure a very weak, high resolution Bragg reflection (30 X-rays) has been recorded with a PHOTON II (left) and a PHOTON III (right). For the PHOTON II noise from dark current is apparent, while for the PHOTON III the background is fully eliminated. The reflection is radially elongated due to Kα1-Kα2 splitting.

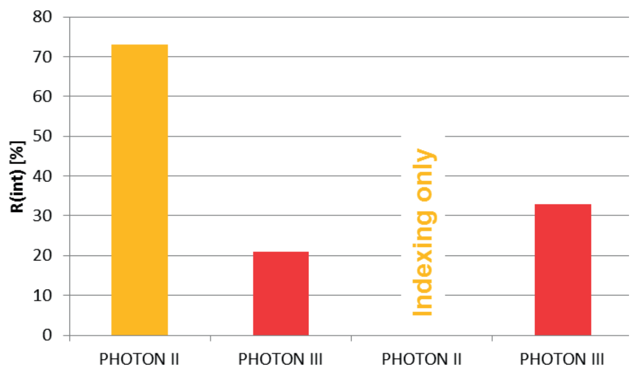


Figure 4: R_{int} values for small and tiny crystals with PHOTON II and PHOTON III detector *Fast Scans*.

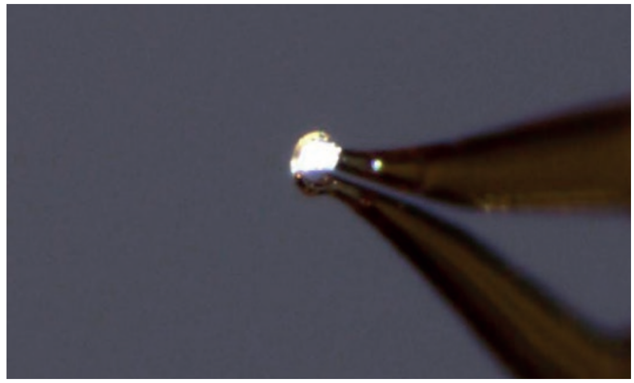


Figure 5a: Picture of the $CaSiF_6{\cdot}2H_2O$ crystal ($10{\times}10{\times}5\mu m^3$).

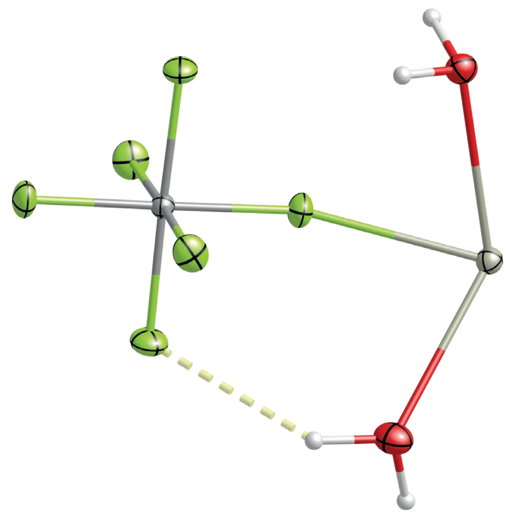


Figure 5b: Crystal structure of $CaSiF_6{\cdot}2H_2O$, asymmetric unit.

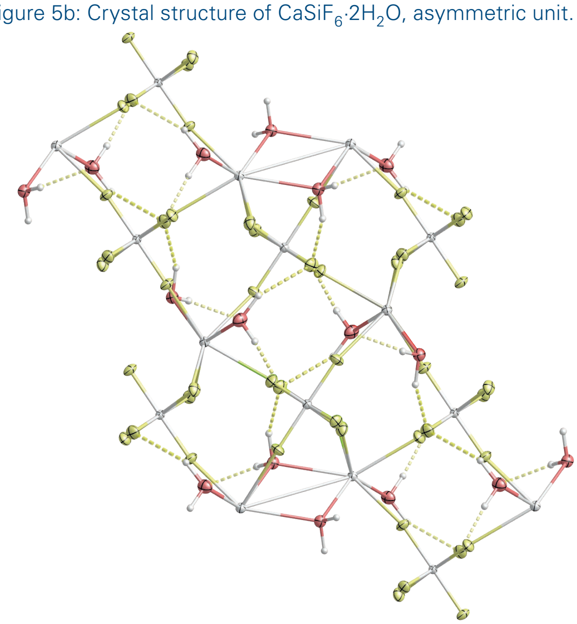


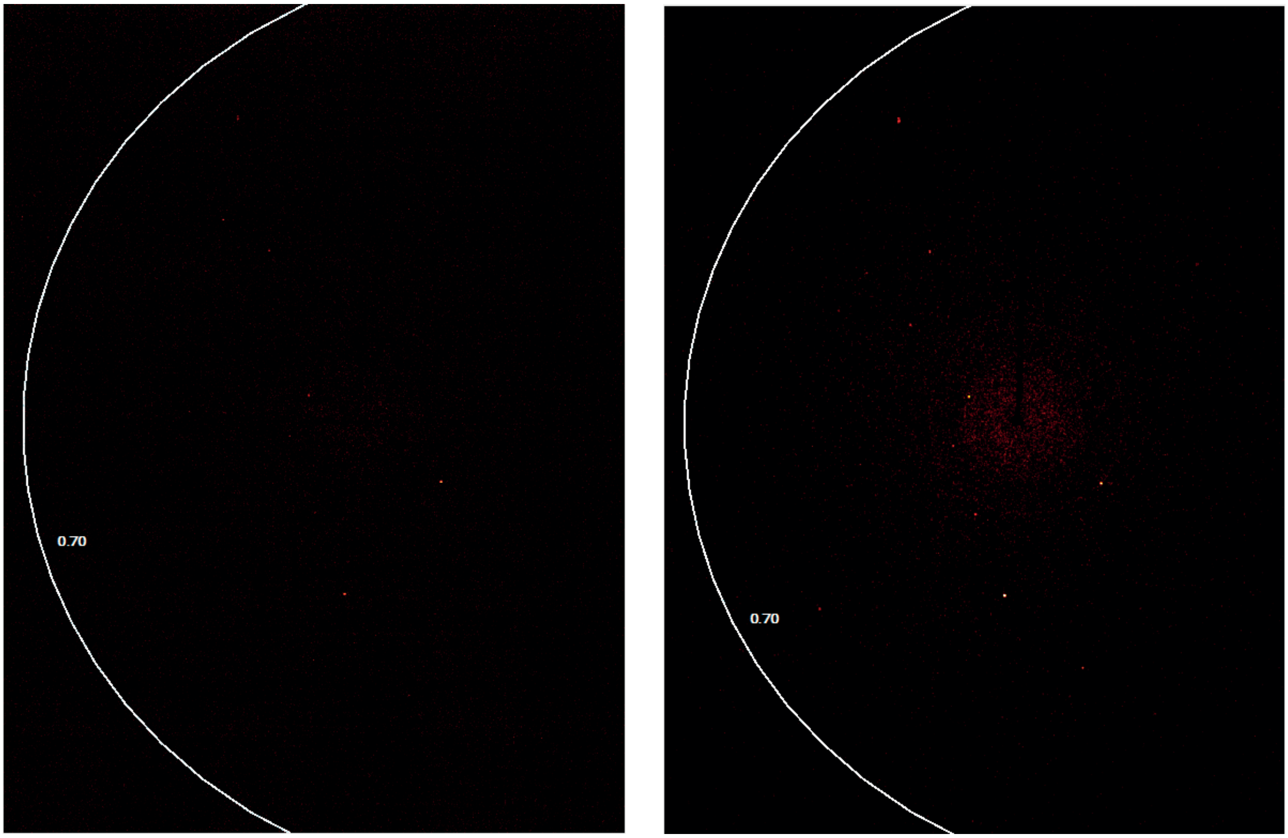
Figure 5c: Crystal structure of $CaSiF_6{\cdot}2H_2O$, unit cell.

Screening and *Fast Scans*

Modern instrumentation, such as the D8 QUEST or the D8 VENTURE (Figure 1), allow quick initial screening of crystals, ensuring a highly efficient use of instrument time. However, in some cases quick screening can equate to a very low diffraction signal. Are quick screening and proper evaluation mutually exclusive? To answer this question, a needle-shaped $10{\times}10{\times}5\ \mu m^3$ ("small") crystal (Figure 5a) and an even smaller $<5{\times}5{\times}5\ \mu m^3$ ("tiny") crystal of $CaSiF_6{\cdot}2H_2O$, both of good quality, were screened with a *Fast Scan*. The *Fast Scan* collects a sphere of data in three minutes with a 180° phi scan with 1°/sec frames. *Fast Scan* data sets were collected for both the PHOTON II and the PHOTON III. Although hardly any signal was visible on the frames, indexing was attempted as well as integrating the data and solving the structure.

The R_{int} statistics (Figure 4) clearly show the superior sensitivity of the PHOTON III photon counting in Mixed-Mode for such extremely weak signals. Correct structures were obtained with the PHOTON III for both crystals with three-minute data (Figures 5b & 5c). For the "tiny" sample data acquired with the PHOTON II, it provided the correct unit cell (Figure 7) but no further processing was possible.

This result demonstrates the superiority of the PHOTON III photon counting in Mixed-Mode as an ideal tool for screening, solving, and evaluating even the tiniest samples in just minutes.



a) b)

Figure 6: One second 0.5° frames for the PHOTON II (a) and PHOTON III (b). Images are on the same scale.

Very weak sample, very low background

To further investigate the potential of the PHOTON III's unique Mixed-Mode and how to best use it, a small crystal of $CaSiF_6 \cdot 2H_2O$ (Figure 5a) was measured with the PHOTON II and the PHOTON III at various exposure times ranging from one second to 15 seconds per frame. Overall, these measurements took between 13 minutes to three hours for the complete data sets.

All data was collected on a D8 VENTURE equipped with a KAPPA goniometer, IµS DIAMOND with Mo Kα microfocus tube and HELIOS optics. Identical data collection strategies with a frame width of 0.5° were used for the various exposure times resulting in 783 frames each. Identical data processing for all data sets yielded 8618 reflections (1661 unique, 100% completeness, multiplicity = 5.2) up to a resolution of 0.70 Å.

$CaSiF_6 \cdot 2H_2O$	$P2_1/n$
a = 5.7210(1) Å	α = 90°
b = 9.1800(2) Å	β = 98.9760(10)°
c = 10.4782(2) Å	γ = 90°
V = 543.871(18) Å³	

Figure 7: Lattice parameters of the $CaSiF_6 \cdot 2H_2O$ crystal.

Diffraction images using one second exposure time for the PHOTON II and the PHOTON III are shown in Figure 6. A careful comparison of the images shows that both detectors feature very low background. While only a few low-resolution reflections are discernible on the PHOTON II frames, the PHOTON III images show intensities to up to 0.7 Å. It should be noted that despite the very short exposure time, even the beamstop shadow is recognizable in middle of the background air scatter (Figure 6b). Statistics of the exposure time-dependent data evaluation are summarized in Figures 8 and 9. The final refinement statistics are excellent for both detectors – even at 1 second exposure time (Figure 9). A closer look, however, clearly reveals the superiority of the PHOTON III detector (Figures 10 & 11). Almost 70% of reflections are considered observed ($I > 2\sigma$), which corresponds to significantly improved R_{int} and $R1_{all}$ values. Not surprisingly, this difference in PHOTON II and PHOTON III detector's data quality is getting smaller with longer exposure time, which might be considered equivalent to more strongly diffracting samples.

The example of weak diffracting samples at short exposure times nicely demonstrates the superiority of the PHOTON III. The PHOTON III achieves the same data quality as the PHOTON II in about one-third of the exposure time. For longer exposure times (which are equivalent to a stronger diffraction signal at shorter exposure time), data quality for both detectors quickly converges.

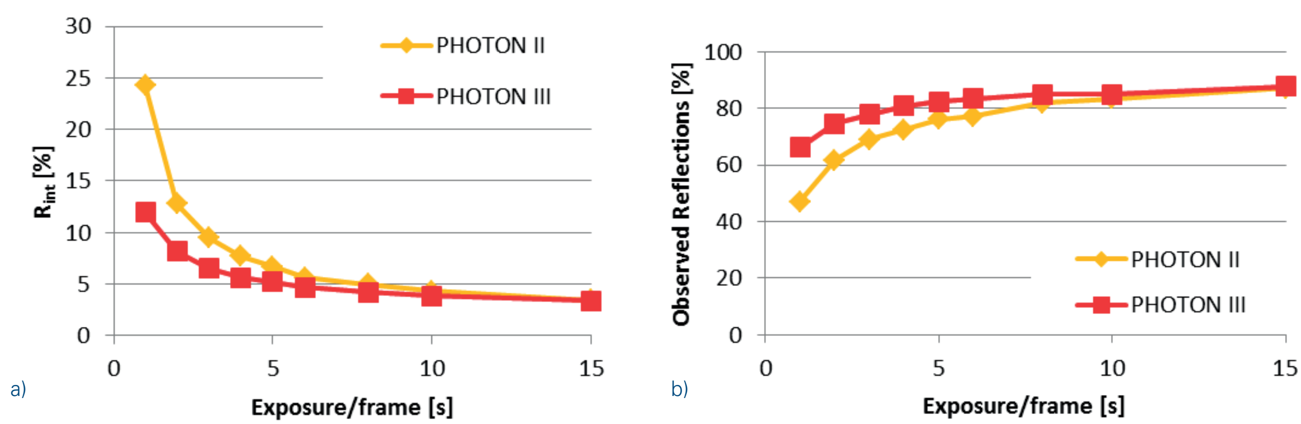


Figure 8: Exposure time/frame a) vs. R_{int} (left) and b) vs. observed reflections indicating the superiority of the PHOTON III data.

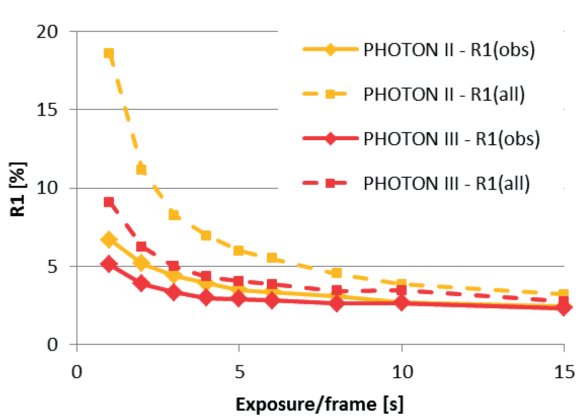


Figure 9: $R1_{obs}$ and $R1_{all}$ indicating the superiority of the PHOTON III.

Overview table of the PHOTON II and PHOTON III data sets

Exp	total	Data from *Fast Scan* [%]	%Obs	R_{int}	R_{sigma}	$R1_{obs}$	$R1_{all}$	$wR2_{all}$	Residuals [e/Å^3]
1s	13 min	0	47.1	24.25	22.56	6.71	18.59	10.42	0.74/-0.79
2s	26 min	0	61.7	12.78	10.87	5.19	11.15	9.08	0.74/-0.62
3s	39 min	0	68.9	9.49	7.48	4.4	8.25	8.42	0.61/-0.54
4s	52 min	0	72.4	7.69	6.32	3.91	6.95	7.67	0.45/-0.51
5s	1:05 h	0	76.0	6.67	5.37	3.5	5.98	6.71	0.49/-0.46
6s	1:18 h	0	77.1	5.61	5.27	3.37	5.49	6.63	0.43/-0.49
8s	1:44 h	0	81.9	4.99	4.03	3.11	4.53	6.33	0.37/-0.43
10s	2:10 h	0	83.3	4.34	3.48	2.69	3.86	5.93	0.38/-0.36
15s	3:15 h	0	87.0	3.43	2.69	2.43	3.22	5.62	0.32/-0.36

Figure 10: Statistics for the PHOTON II data.

Exp	total	Data from *Fast Scan* [%]	%Obs	R_{int}	R_{sigma}	$R1_{obs}$	$R1_{all}$	$wR2_{all}$	Residuals [e/Å^3]
1s	13 min	0.0	66.2	11.92	9.38	5.12	9.08	12.81	0.78/-0.67
2s	26 min	0.6	74.64	8.14	6.24	3.87	6.25	8.13	0.55/-0.67
3s	39 min	1.7	77.83	6.52	4.83	3.32	4.97	7.16	0.47/-0.43
4s	52 min	3.8	80.72	5.62	4.39	2.98	4.34	6.75	0.5/-0.41
5s	1:05 h	4.1	82.3	5.22	3.93	2.92	4.03	6.33	0.37/-0.41
6s	1:18 h	5.3	83.38	4.68	3.55	2.83	3.86	6.44	0.43/-0.35
8s	1:44 h	5.3	84.89	4.21	3.14	2.62	3.42	6.02	0.37/-0.30
10s	2:10 h	5.3	84.89	3.87	3.14	2.67	3.47	6.14	0.32/-0.40
15s	3:15 h	5.3	87.78	3.36	2.37	2.32	2.75	5.52	0.38/-0.30

Figure 11: Statistics for the PHOTON III data.

Conclusion

Based on several data sets obtained from a small, good quality $CaSiF_6 \cdot 2H_2O$ crystals, we demonstrate the PHOTON III's unique capability to collect best-quality data. Mounted on a D8 QUEST (Figure 12) or D8 VENTURE (Figure 13) we have solutions, ideal for quick initial screening and complete data collection on weak diffracting crystals.

The photon-counting Mixed-Mode technology employed in the PHOTON III detector ensures outstanding data quality for even the weakest diffractors. The comparative analysis of a series of data sets with various exposure times presented clearly demonstrates the impact of the PHOTON III photon counting capabilities. Best data quality without sacrificing data completeness or data collection time is achieved by combining photon counting data with a *Fast Scan*.

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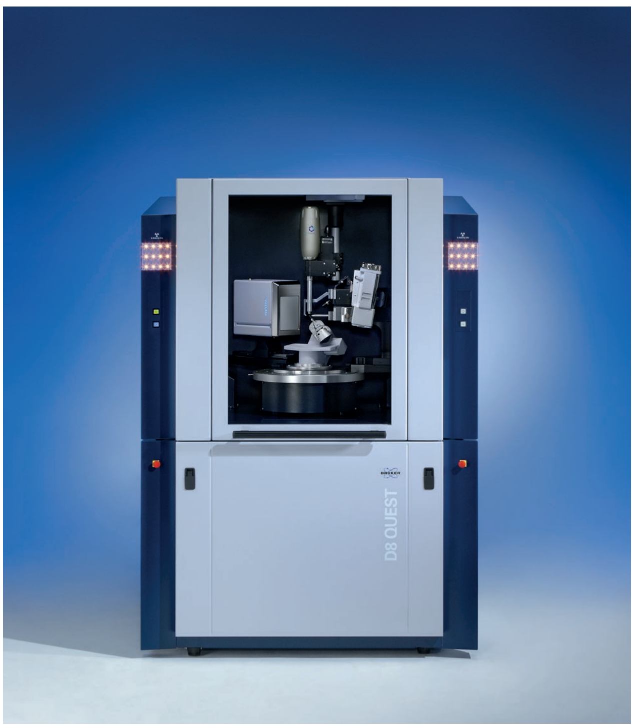

Figure 12: D8 QUEST with PHOTON III 14 and sealed tube with TRIUMPH monochromator.

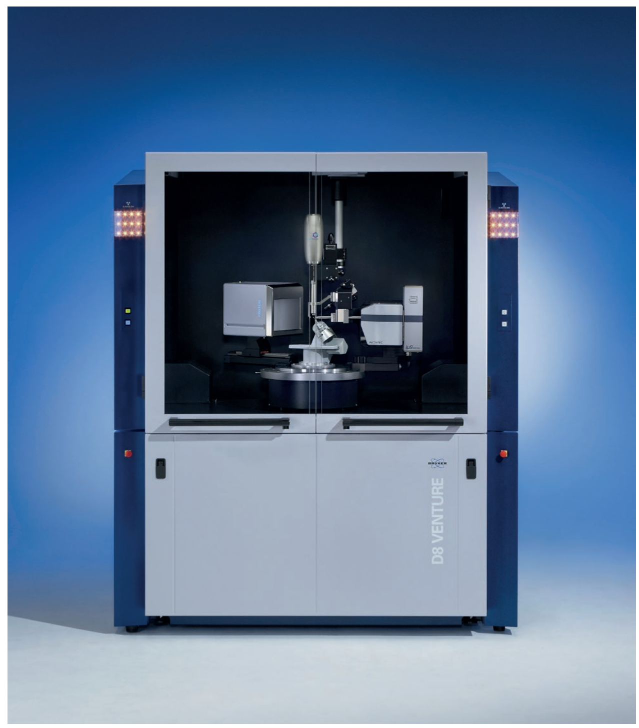

Figure 13: D8 VENTURE with PHOTON III 28 and IμS 3.0 source.

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