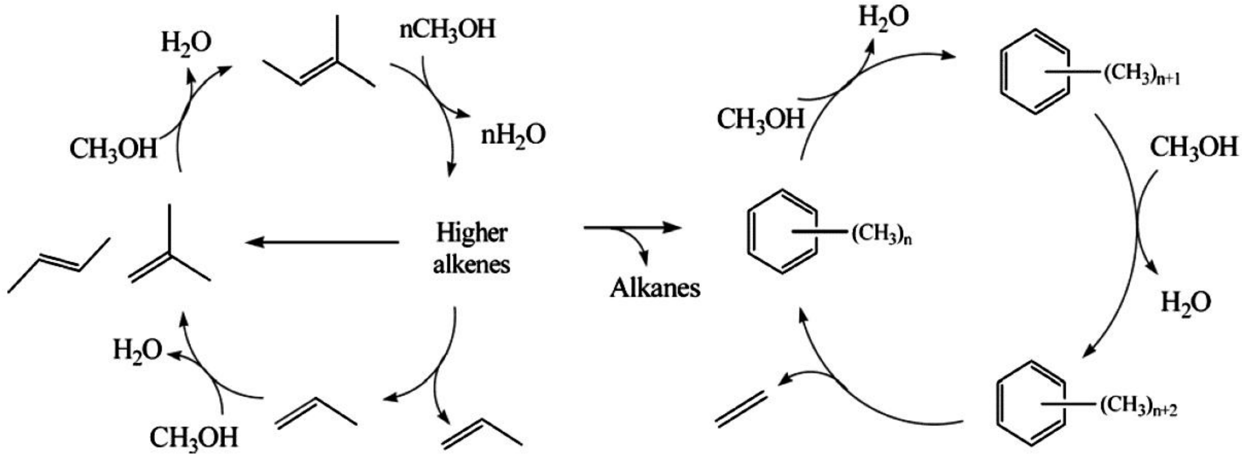
Combined *in situ* solid-state NMR, UV/Vis, and on-line GC studies of heterogeneously catalyzed reactions under continuous flow conditions

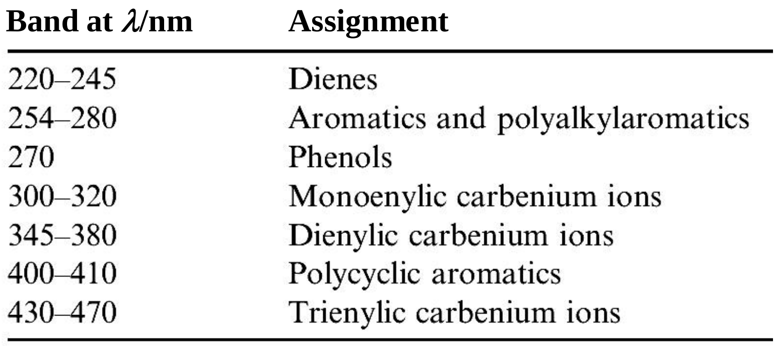
Spectroscopic background: The *in situ* flow MAS NMR technique (see Topic 3 of link "*In Situ* Solid-State NMR Techniques") allows investigations of **the steady state of heterogeneously catalyzed reactions**, which is particularly interesting if **catalytically active deposits** contribute to the mechanism of these reactions. One of the heterogeneously catalyzed reactions being in the focus of research is the **methanol-to-olefin (MTO)** conversion and, more recently, the **methanol-to-propene (MTP)** conversion on Broensted acidic catalysts. Methanol is primarily derived from natural gas, where steam reforming converts the various light hydrocarbons in natural gas (primarily methane) into carbon monoxide and hydrogen. Subsequently, methanol is produced by hydrogenation of carbon monoxide. Via the MTO and MTP conversion on zeolites, a broad variety of olefins can be obtained, depending on the structure type and acid sites of the catalyst as well as the reaction conditions [1-13].

Scheme 1 shows a concept for the conversion of **methanol-to-hydrocarbons (MTH)** over zeolite H-ZSM-5, which is named **dual-cycle mechanism** [3]. While for zeolite H-ZSM-5 with a crossing 10-ring pore system the olefin-based cycle (left) dominates, the aromatic-based cycle (right) plays an important role in zeolite catalysts with small cages and small cage windows, such as SAPO-34 (cage diameter of ca. 0.94 nm and diameter of the 8-ring windows of ca. 0.38 nm) [2].



Scheme 1

Large **olefins and alkylated aromatics** contributing to the dual-cycle mechanism have a **long residence time in the catalyst pores and cages** and, therefore, are available for ***in situ* continuous flow (CF) MAS NMR spectroscopy, combined with on-line gas chromatographic (GC) analysis** of the volatile reaction products [14-19]. Furthermore, UV/Vis spectroscopy is sensitive for numerous of these hydrocarbon-pool compounds, such as dienes, aromatics, and carbenium ions (**Table 1**) [18]. Therefore, the above-mentioned *in situ* technique was **additionally combined with *in situ* UV/Vis spectroscopy** (see Sections "flow probe 2" and "flow probe 3", accessible via link "*In Situ* Solid-State NMR Techniques") for studies of the methanol conversion on Broensted acidic zeolite catalysts [16, 18, 19].



Band at λ/nm	Assignment
220–245	Dienes
254–280	Aromatics and polyalkylaromatics
270	Phenols
300–320	Monoenylic carbenium ions
345–380	Dienylic carbenium ions
400–410	Polycyclic aromatics
430–470	Trienylic carbenium ions

Table 1

Fig. 1 shows *in situ* ^{13}C MAS NMR and *in situ* UV/Vis spectra recorded during the conversion of ^{13}C-enriched methanol on the silicoaluminophosphate H-SAPO-34 under continuous-flow conditions at reaction temperatures of T = 473 (a) to 673 K (d) [18]. The yields of volatile reaction products, such as dimethyl ether (DME), ethene ($C_{2=}$), propene ($C_{3=}$), and butenes ($C_{4=}$), were simultaneously analyzed by on-line GC and are given on the left-hand side of **Fig. 1**.

At temperatures of T = 473 K and 523 K (**Figs. 1a and 1b**), the conversion of methanol is dominated by the formation of DME. This is indicated by the on-line GC data and by the ^{13}C MAS NMR signals of adsorbed methanol at δ_{13C} = 50 ppm and DME at δ_{13C} = 61 ppm (**Table 2** [18]). The simultaneously recorded UV/Vis spectra of organic compounds formed during the methanol conversion are depicted on the right-hand side. Already at T = 473 K, UV/Vis sensitive species begin to be formed, causing a band of dienes at λ = 245 nm (**Table 1**). The concentration of these dienes is too small for their detection by ^{13}C MAS NMR spectroscopy.

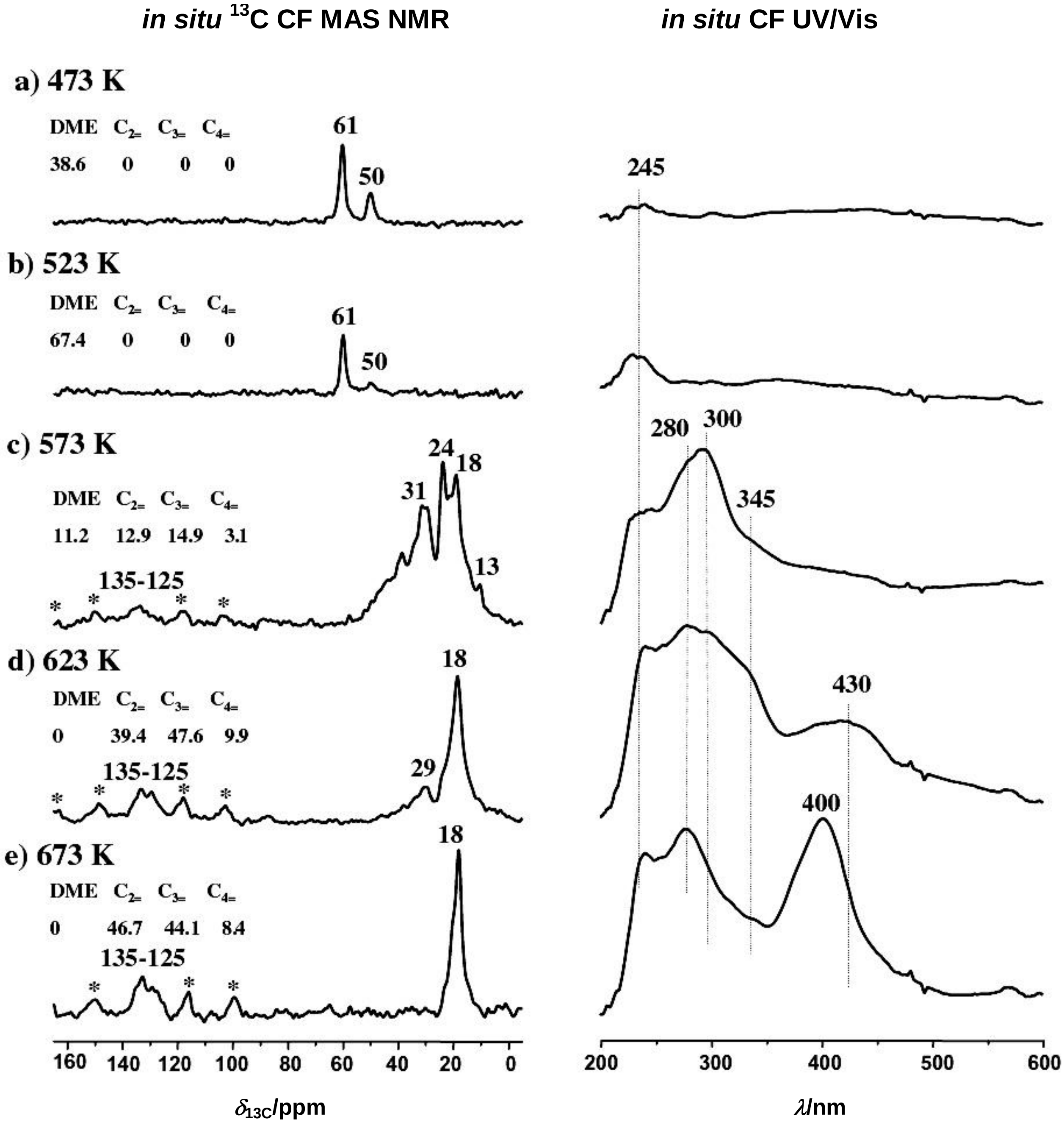


Fig. 1

Signal at δ_{13C}/ppm	Assignment	Concentration of ^{13}C atoms/mmol g^{-1}		
		In situ CF at 623 K	*In situ* CF at 673 K	N_2 at 673 K
16–21	In methyl groups bound to aromatics	1.87	0.53	0.31
14–15 and 22–29	In ethyl groups bound to aromatics	0.42	0.16	0.06
23–24 and 33–37	In isopropyl groups bound to aromatics	0.45	–	–
125–135	In alkylated and non-alkylated aromatics	3.28	3.33	2.45
145–155	At ring positions of aromatics bound to hydroxyl groups	–	–	–

Table 2

At T = 573 K (**Fig.1c**), most of the methanol and DME molecules are converted. New ^{13}C MAS NMR signals appear at δ_{13C} = 10 to 40 ppm and δ_{13C} = 125 to 135 ppm, which indicate the formation of polyalkylaromatics. Simultaneously, a strong increase of the yields of light olefins was observed by on-line GC analysis. The *in situ* UV/Vis spectrum recorded at T = 573 K consists of a dominating band at λ = 300 nm due to the formation of monoenylic carbenium ions (**Table 1**). Furthermore, additional bands appear as weak shoulders at λ = 280 nm and 345 nm, attributed to polyalkylaromatics and dienylic carbenium ions (**Table 1**). These findings indicate that olefinic compounds react with monoenylic carbenium ions to dienylic carbenium ions and aromatic compounds.

At T = 623 K (**Fig. 1d**), a further increase of the yields of light olefins, but no DME were found by on-line GC analysis. The ^{13}C MAS NMR spectrum is dominated by a signal at δ_{13C} = 18 ppm due to methyl groups bound to aromatics, while most of the other signals in the region of alkyl groups occurring at lower reaction temperatures disappeared. Simultaneously, the intensities of the ^{13}C MAS NMR signals of aromatic compounds at δ_{13C} = 125 to 135 ppm increased. The UV/Vis spectrum recorded at T = 623 K is dominated by a band at λ = 280 nm with shoulders at λ = 300 and 345 nm due to polyalkylaromatics and monoenylic and dienylic carbenium ions, respectively. In addition, a broad band appeared at λ = 430 nm, which is generally explained by trienylic carbenium ions (**Table 1**).

The *in situ* UV/Vis spectra recorded at T = 573 to 623 K hint at a reaction of olefins with reactive carbenium ions leading to higher carbenium ions with a maximum of three conjugated double bonds. Up to the formation of dienylic carbenium ions, this pathway may contribute to the formation of aromatic hydrocarbon-pool compounds. The presence of trienylic carbenium ions is an indication for the formation of larger organic compounds, such as carbenium ions formed by polycyclic aromatics. In agreement with the above-mentioned finding, the *in situ* UV/Vis spectrum recorded at T = 673 K (**Fig. 1e**) shows a strong band at λ = 400 nm due to non-protonated polycyclic aromatics, such as polymethylanthracenes. The bands of carbenium ions at λ = 345 nm and 430 nm decreased, and at low wavelengths exclusively bands of dienes and polyalkylaromatics appear at λ = 245 nm and 280 nm, respectively. The simultaneously recorded *in situ* ^{13}C MAS NMR spectrum consists of signals at δ_{13C} = 18 ppm and ca. 135 ppm (**Fig. 1e, left**), which are caused by polymethylaromatics

(**Table 2**). In agreement with the results of UV/Vis spectroscopy, the broad ^{13}C MAS NMR signal at δ_{13C} = 125 ppm indicates the formation of polycyclic aromatics.

In **Fig. 2a, left**, the ^{13}C MAS NMR spectrum of H-SAPO-34 recorded at room temperature after methanol-to-olefin conversion at T = 673 K for 3 h (used H-SAPO-34 catalyst) is shown. The concentration of organic deposits in the chabazite cages ($T_{12}O_{24}$: 1.38 mmol/g) of H-SAPO-34 was determined by simulation of the ^{13}C MAS NMR signals caused by ^{13}C atoms in alkyl groups and aromatic rings and the comparison of these intensities with an external intensity standard (dehydrated H-SAPO-34 loaded with $^{13}CH_3OH$).

In **columns 3 and 4 of Table 2**, the concentration of ^{13}C atoms contributing to alkyl groups and aromatic rings of organic deposits, formed on H-SAPO-34, are given. Upon methanol conversion at T = 623 K, aromatic compounds with 3.28 mmol ^{13}C atoms corresponding to 0.55 mmol aromatic rings per gram were formed, which are ca. 0.4 benzene rings per chabazite cage. These aromatic compounds are alkylated by a mean number of 2.23 mmol methyl, ethyl, and propyl groups per gram corresponding to ca. 4.1 alkyl groups per aromatic ring.

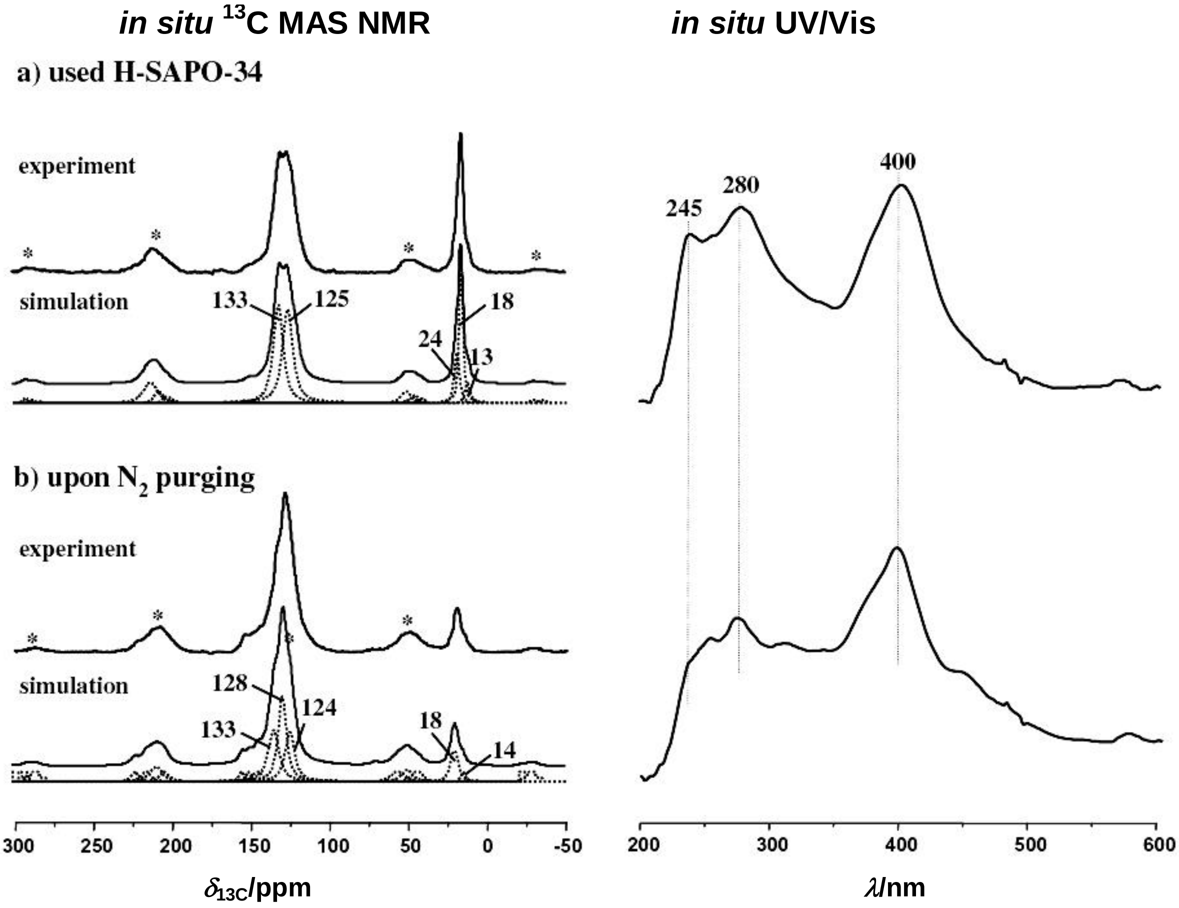


Fig. 2

After increasing the reaction temperature to T = 673 K, a strong decrease of the mean number of alkyl groups to 0.61 mmol/g corresponding to 1.1 alkyl groups per aromatic ring occurred, while the number of aromatic rings per cage was nearly constant (**column 4 of Table 2**). The **decrease of the yield of propene at the reaction temperature of T = 673 K is explained by the lower number of methyl groups per aromatic ring** of the hydrocarbon pool compounds in comparison with the hydrocarbon pool compounds present at T = 623 K.

In order to study the thermal stability of the organic deposits formed on H-SAPO-34 at T = 673 K, the methanol flow was stopped and the used catalyst was purged with dry nitrogen gas at T = 673 K for 2 h. **Fig. 2b, left**, shows the ^{13}C MAS NMR spectrum of this purged catalyst, recorded at room temperature for quantitative evaluation. The result of the evaluation is summarized in **column 5 of Table 2**. As indicated by these values, the number of ^{13}C atoms in aromatic compounds decreased slightly to 2.45 mmol/g corresponding to *ca.* 0.3 aromatic rings per chabazite cage. Also the number of alkyl groups decreased to 0.34 mmol/g corresponding to 0.8 alkyl groups per aromatic ring. This is a decrease of organic deposits by 25 to 27% in comparison with the used catalyst before purging with dry nitrogen gas at T = 673 K. In the UV/Vis spectra of the purged H-SAPO-34 catalyst, mainly the UV bands of polyalkyl aromatics at λ = 280 nm and a shoulder at λ = 245 nm due to dienes are decreased (compare **Figs. 2a and 2b, right**). This behavior corresponds to the smaller number of polyalkylaromatics observed by ^{13}C MAS NMR spectroscopy. On the other hand, the large band at λ = 400 nm indicates that the polycyclic aromatics occurring in the cages of used H-SAPO-34 catalyst have a high thermal stability and are not affected by purging with nitrogen (**Fig. 2b, right**). Hence, these **polycyclic aromatics are the reason for the catalyst deactivation at high reaction temperatures**.

Catalyst preparation: The silicoaluminophosphate H-SAPO-34 had an $n_{Si}/(n_{Al} + n_{Si} + n_P)$ ratio of 0.11 and was synthesized as described in Ref. [20]. Before the use of this zeolite for *in situ* flow experiments, a dehydration was performed with the sample material in a “sample tube system 1” at “vacuum line 1” (see Sections “sample tube system 1” and “vacuum line 1”, accessible via link “*In Situ* Solid-State NMR Techniques”). This treatment starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to T = 393 K within 2 hours. At this temperature, the sample was dehydrated for 2 hours. Subsequently, the temperature was increased up to T = 723 K within 3 hours and evacuated at this temperature for 12 hours. Finally, the sample tube system was closed via the vacuum valve and disconnected from the vacuum line (after this line was ventilated with air). The transfer of the dehydrated sample into the MAS NMR rotor was performed without air contact in a mini glove box (see Section "mini glove box", accessible via link "*In Situ* Solid-State NMR Techniques"), purged with dry nitrogen gas.

***In situ* studies:** The *in situ* ^{13}C stopped-flow MAS NMR spectra in Figs. 1 and 2 were recorded using the equipment described in Section "equipment 1" and a 7 mm high-temperature MAS NMR probe of Doty Scientific Instruments, modified as described in Section "flow probe 3", both accessible via link "*In Situ* Solid-State NMR Technique".

Via an exhaust tube on top of the MAS NMR rotor, the NMR probe was connected with the sampling loop of a gas chromatograph HP 5890 (Hewlett–Packard) equipped with a Coating Poraplot Q capillary column (Chrompack Plot fused silica, length 50 m, inner diameter 0.32 mm). The exhaust flow containing the volatile reaction products was sampled and analyzed in steps of 15 min. A constant flow of methane (8 ml/min), added to the methanol feed, was used as an internal GC standard and allowed a quantification of the reaction products.

High-power proton decoupled (HPDEC) ^{13}C MAS NMR spectra were recorded at a Bruker MSL 400WB spectrometer at the resonance frequency of ν_0 = 100.6 MHz and after excitation with $\pi/2$ pulses. Applying an external intensity standard consisting of dehydrated H-SAPO-34 loaded with $^{13}CH_3OH$, ^{13}C spin-counting was performed with the repetition time of 30 s. All ^{13}C MAS NMR spectra were referenced to tetramethylsilane (TMS).

At the bottom of the 7 mm MAS NMR rotor, a quartz glass window was installed. Via this quartz glass window and using a fiber optics, the catalyst inside the rotor was investigated by a fiber-optics UV/Vis spectrometer. Reference UV/Vis spectra of calcined H-SAPO-34 were recorded at the reaction temperature prior to introducing reactants. *In situ* UV/Vis measurements were recorded in the diffuse reflection mode between λ = 200 and 600 nm and using an HPSUV1000A Fiber Optics spectrometer, an AvaLight-DH-S deuterium light source, and a fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes.

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