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# Optical technology for detecting the decomposition products of SF<sub>6</sub>: a review

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**Abstract.** Studies have demonstrated that partial discharge in SF<sub>6</sub>-insulated electrical equipment can cause SF<sub>6</sub> decomposition, resulting in the generation of various products. Quantitative detection of these decomposition products can be used to evaluate the state of the equipment's insulation. The use of optical methods for detecting the products has many advantages, such as high precision, fast response, and sample reusability. Thus far, optical detection methods have been applied for detection of SF<sub>6</sub> decomposition products, and a few promising results have been obtained. We review the various optical technologies for detection of SF<sub>6</sub> decomposition products, introduce their principles and applications, and summarize some recent research progress. In addition, we propose two optical detection technologies that can be applied in this field. © 2018 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.OE.57.11.110901](https://doi.org/10.1117/1.OE.57.11.110901)]

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## 1 Introduction

Sulfur hexafluoride (SF<sub>6</sub>) is a reliable insulating gas and has excellent arc-extinguishing properties. SF<sub>6</sub>-insulated electrical equipment, such as switchgear, transformers, and lines, is widely used in city power grids and ultrahigh-voltage power transmission systems owing to its small footprint, high reliability, and long service life. Safe and stable operation of SF<sub>6</sub>-insulated electrical equipment is crucial for effective power supply. However, during the production, installation, and maintenance of SF<sub>6</sub>-insulated electrical equipment, insulation defects such as burrs and metal particles inevitably appear inside the equipment. Over long-term operation, these defects lead to partial discharge (PD). PD can cause decomposition of SF<sub>6</sub> gas, resulting in the production of various low-fluorine sulfides, such as SF<sub>4</sub>, SF<sub>3</sub>, SF<sub>2</sub>, and S<sub>2</sub>F<sub>10</sub>.<sup>1-3</sup> Because of the presence of trace impurities, such as H<sub>2</sub>O and O<sub>2</sub>, in the equipment, these low-fluorine sulfides generate many more stable decomposition products, such as SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S. Simultaneously, PD damages the solid insulation of the equipment, causing it to react with SF<sub>6</sub> to produce CS<sub>2</sub>, CF<sub>4</sub>, and other decomposition products.<sup>4-6</sup> Without accurate detection of these products, defects in the equipment cannot be detected early. PD gradually develops and leads to deterioration of the equipment's insulation. Eventually, its effects may even threaten the safe operation of the entire power grid.

Extant studies show that the components and formation rates of SF<sub>6</sub> decomposition products due to different types of insulation defects are related to the insulation defect type and its severity.<sup>7,8</sup> The detection of SF<sub>6</sub> decomposition products can help in assessment of the type and severity of insulation defects. Therefore, researchers in power industry hope to adopt effective detection of SF<sub>6</sub> decomposition

products to ensure timely detection of insulation defects in the equipment.<sup>9-13</sup>

The methods of SF<sub>6</sub> decomposition products detection can be divided into chemical and optical methods. Chemical detection employs adsorption, separation, and other methods and the various physical and chemical properties of different products to detect decomposition product concentrations. The commonly used chemical detection methods are gas chromatography (GC), detection tubes, and gas sensitivity sensors, as listed in Table 1.<sup>14-20</sup>

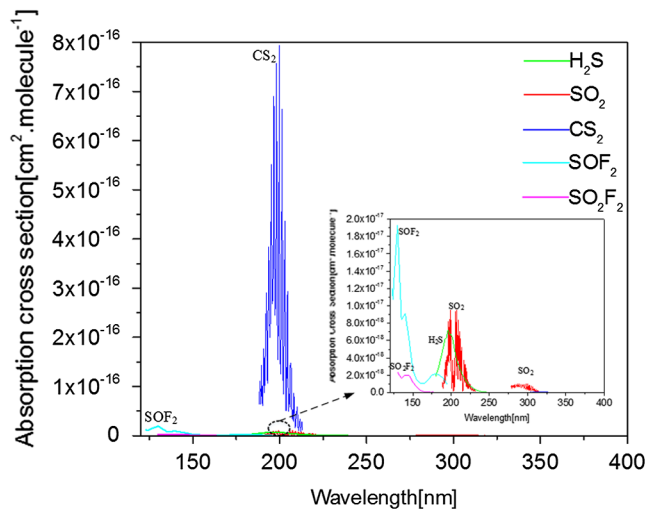
GC with high sensitivity is costly, time-consuming, and suitable for laboratory-based analysis rather than continuous on-line monitoring or portable detection. A detection tube can be used to detect major decomposition products, such as SO<sub>2</sub> or HF, at parts per million (ppm) levels. However, detection tubes have poor accuracy because the concentration of decomposition products is determined by color changes, making these tubes unsuitable for on-line monitoring.<sup>21</sup> A gas-sensitivity sensor can be connected to the equipment to achieve online monitoring or portable detection. However, the sensor has poor gas selectivity and is easy to be contaminated.

Optical detection is based on spectral analysis technology, which has been widely used in many fields, such as environmental science, medical treatment, chemical engineering, and food science. Most SF<sub>6</sub> decomposition products have absorption characteristics in both infrared (IR) and ultraviolet (UV) spectra. In different regions, the absorption characteristics are different. For example, Fig. 1 shows the absorption spectrum of the partial decomposition products of SF<sub>6</sub> in the UV region. The strong absorption characteristic in the 190- to 210-nm band corresponds to CS<sub>2</sub>. If we use UV spectroscopy to detect this product, the detection precision can be improved. However, in the 190- to 210-nm band, interference from H<sub>2</sub>S and SO<sub>2</sub> is present and must be eliminated. Figure 2 shows the absorption spectrum of the partial decomposition products of SF<sub>6</sub> in the IR region. There is very little overlap among the spectra of the decomposition

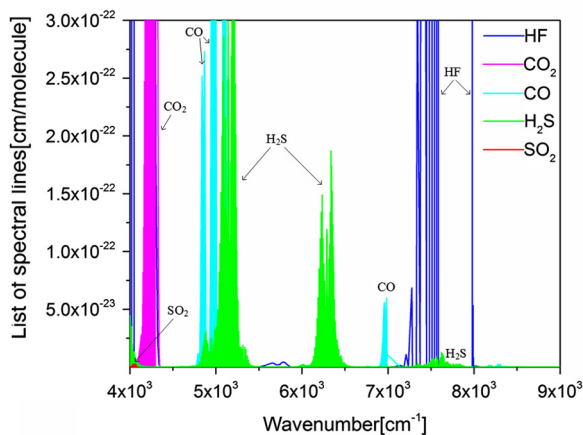
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**Table 1** Commonly used chemical detection methods.

Method	Accuracy	Speed	Anti-interference	Range	Portability
GC	ppb	Complex operation, slow detection speed	Strong anti-interference ability	Most decomposition products	Just suitable for laboratory testing
Detection tube	ppm	By color comparison, fast detection speed	Easily affected by cross-interference	Partial products, such as SO <sub>2</sub> , HF, and other strong acid substances	Simple structure, easy to carry
Gas-sensitivity sensor	ppm	Calculate through the change of sensor resistance, fast detection speed	Poor gas selectivity, easy to be contaminated	SO <sub>2</sub> , SOF <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , and H <sub>2</sub> S	Good portability



**Fig. 1** The absorption spectra of the partial decomposition of SF<sub>6</sub> in UV. All data come from The MPI-Mainz UV/VIS Spectral Atlas, which is a comprehensive collection of cross sections for gaseous molecules and radicals. H<sub>2</sub>S, WuChen (1998), 295 K, 160 to 260 nm; SO<sub>2</sub>, Danielache (2008), 293 K, 183 to 350 nm; CS<sub>2</sub>, Ahmed Kumar (1992), 300 K, 188 to 231 nm; SOF<sub>2</sub>, Pradayrol (1996), 298 K, 123 to 195 nm; SO<sub>2</sub>F<sub>2</sub>, Pradayrol (1996), 298 K, 130 to 210 nm.



**Fig. 2** The absorption spectra of the partial decomposition of SF<sub>6</sub> in IR. All data come from HITRAN on the Web, 296 K, 1 atm.

products. We can exploit this feature to detect products using laser light sources of specific wavelengths to effectively eliminate interference from other products.

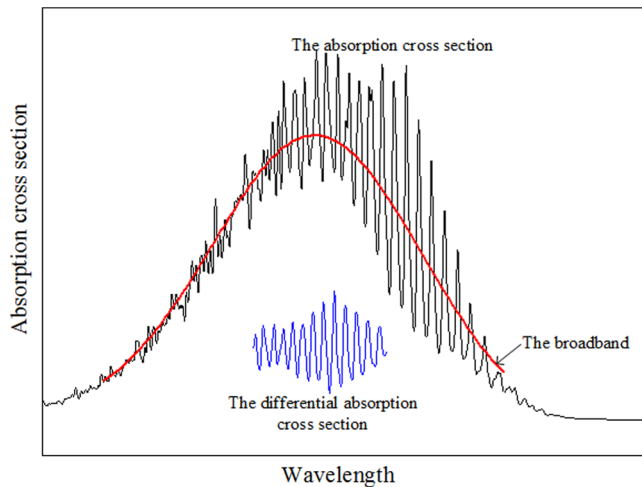
Compared with chemical detection, optical detection has many advantages such as fast response, high sensitivity, only requiring a small sample, and sample reusability. Most of the main SF<sub>6</sub> decomposition products can be detected optically. Moreover, optical detection can fulfill all requirements of gas detection devices in the power industry, including on-line monitoring and portable detection. Detection devices based on UV spectroscopy and fluorescence spectroscopy can be modularized, have a compact structure, and are portable.<sup>22,23</sup> Fourier transform infrared spectrometry (FTIR) and photoacoustic spectroscopy (PAS) have been used for the on-line monitoring of certain gases.<sup>24–27</sup> In summary, optical detection has considerable application potential for the detection of SF<sub>6</sub> decomposition products.

So far, numerous studies regarding the detection of SF<sub>6</sub> decomposition products have been conducted that have employed IR and UV spectroscopy, such as IR spectroscopy, UV fluorescence, and PAS. These studies have obtained some relevant results. However, most have focused on a specific method without providing an overview of the various optical detection methods. Therefore, herein, we comprehensively review the application of optical detection technologies for detecting SF<sub>6</sub> decomposition products according to UV and IR spectroscopy. In addition, we propose two methods that can be applied in this field.

## 2 UV Spectroscopy

### 2.1 Differential Optical Absorption Spectroscopy

Differential optical absorption spectroscopy (DOAS) was proposed by NOXON<sup>28</sup> in the early 1980s. Platt and Perner<sup>29,30</sup>—at the Institute of Environmental Physics, Heidelberg University, Germany—extended the technology to research on the tropospheric atmosphere. The principle of DOAS involves separating the broadband and narrowband spectral structures in an absorption spectrum to isolate the narrow target gas absorption.<sup>31</sup> In the absorption spectrum, the influence of Rayleigh scattering, Mie scattering, and turbulence causes very broad or smooth spectral characteristics, whereas the target gas exhibits narrowband absorption structures. In Fig. 3, the black line denotes the absorption cross section, which contains the broadband and narrowband features, whereas the red line denotes the broadband feature separated from the absorption cross section. The inset with the blue line illustrates the differential absorption



**Fig. 3** Differential spectrum schematic. The black line is the absorption cross section, which contains the broad- and narrowband; the red line is the broadband that is separated from the absorption spectrum; the blue line is the differential absorption cross section.

cross section, which only contains the absorption feature of the target gas.

In DOAS, the influence of spectral absorption caused by Rayleigh scattering and Mie scattering can be effectively eliminated, and the differential spectrum that only reflects the absorption feature of the target gas is obtained. Moreover, when electronic transitions occur in the UV region, they are accompanied by molecular vibrational and rotational energy transitions. Spectral intensity in UV spectra is several orders of magnitude higher than that in IR spectra. Therefore, this technology has high detection precision.

The decomposition products of SF<sub>6</sub> that have absorption characteristics in UV spectroscopy are mainly SO<sub>2</sub>, H<sub>2</sub>S, and CS<sub>2</sub>. These products have been investigated in other fields, such as atmospheric chemistry and environmental engineering. The researchers in these fields have attempted to achieve high-sensitivity and portable monitoring.<sup>32–34</sup> Vita et al.<sup>32</sup> could design and construct a lightweight, portable, and low-power long-path DOAS instrument for use at remote locations, specifically to measure the degassing from active volcanic systems, due to the developments in fiber-coupling telescope technology and the availability of UV light-emitting diodes (LEDs). Their instrument could measure SO<sub>2</sub> and potentially other trace gases through long open paths around volcanic vents. The instrument's SO<sub>2</sub> detection limit was 8 ppm. Degner et al.<sup>33</sup> developed a set of optical sensing systems employing an LED lamp as a light source. Compared with the traditional deuterium and xenon light sources, the LED light source is cheaper, longer lasting, more stable, and more suitable for local and on-line monitoring. The detection limits of SO<sub>2</sub> and NO<sub>2</sub> were 1 ppm, and the detection limit of O<sub>3</sub> reached 30 parts per billion (ppb). Nasse et al.<sup>34</sup> used a laser-driven light source instead of the traditional Xe arc lamp and an optical fiber bundle in the telescope for the transmission and reception of the measurement signal to obtain autonomous long-term trace gas measurements. These improvements enhanced the wavelength-selective coupling from the light source into the fiber, which reduced stray light. Moreover, the coupling and configuration of the optical fiber was optimized compared with

previous designs to maximize light throughput and reduce stray light.

The open paths have been used to increase the optical length in the applications.<sup>32–34</sup> However, these applications are unsuitable for detecting the decomposition products of SF<sub>6</sub>. The SF<sub>6</sub>-insulated electrical equipment is enclosed. A suitable option for detecting gas in the equipment involves introducing the gas into a gas cell, which is integrated into the portable device. Zhang et al.<sup>35</sup> reported a UV-DOAS device for detecting SF<sub>6</sub> decomposition products with a portable design, and the schematic diagram is shown in Fig. 4. The device mainly comprised a light source, gas cell, spectrometer, and laptop. The differential absorption spectrum of SO<sub>2</sub> was obtained by performing Sym14 wavelet-layering treatment. The SO<sub>2</sub> concentration was calculated according to the characteristic peak obtained through fast Fourier transformation in the 190- to 230-nm and 290- to 310-nm bands. The results showed that the device had a lower detection limit in the 190- to 230-nm band than in the 290- to 310-nm band, and the detection limit was 132.4 ppb with signal-to-noise ratio (SNR) = 3.

Zhang et al.<sup>36</sup> also investigated the quantitative detection of CS<sub>2</sub> using this device. The detection limit is 8.65 ppb in the 190- to 210-nm band. However, Fig. 2 shows that an absorption spectrum of SO<sub>2</sub> continues to exist in this band. To avoid interference of this product, the absorption spectrum of the 290- to 310-nm band can be used to detect the SO<sub>2</sub> concentration initially. Then, the interference of SO<sub>2</sub> can be deducted to obtain the exact concentration of CS<sub>2</sub> in the 190- to 210-nm band, as shown in Fig. 5.

Few studies have been conducted on the detection of H<sub>2</sub>S based on UV-DOAS. Zhang et al.<sup>37</sup> established the relationship between the concentration of H<sub>2</sub>S and its UV absorption spectrum using wavelet transform and frequency-domain analysis. In addition, they studied in detail the overlap of H<sub>2</sub>S and CS<sub>2</sub> in the 190- to 210-nm band. H<sub>2</sub>S absorption in the wave number domain was discovered to be affected by CS<sub>2</sub> and cannot be quantitatively analyzed directly by inversion. However, CS<sub>2</sub> absorption in the wave number domain remains unaffected, which means that CS<sub>2</sub> concentration can be determined, as shown in Fig. 6. The influence of CS<sub>2</sub> on H<sub>2</sub>S was determined experimentally to confirm the corrected inversion formula, and thus, quantitative measurement of mixed CS<sub>2</sub> and H<sub>2</sub>S gas was realized.

Through multiple studies on portable detection devices for SF<sub>6</sub> decomposition products, Zhang et al. quantitatively detected SO<sub>2</sub>, H<sub>2</sub>S, and CS<sub>2</sub> in the SF<sub>6</sub>-insulated electrical equipment. The detection device is low cost, with simple structure, and reliable sensitivity, which makes it suitable for applications in the power industry.

## 2.2 UV Fluorescence Method

The UV fluorescence method is a gas quantification method based on detection of the intensity of the fluorescence spectrum emitted by a gas molecule returning to its ground state from an excited state. After a molecule absorbs excitation light of a certain wavelength, it returns to its lowest excited energy level through vibration relaxation and subsequently transitions downward to generate fluorescence.<sup>38</sup> The wavelength of the fluorescence is generally longer than that of the excitation light. Fluorescence can be measured with a very low background signal so long as the excitation light is

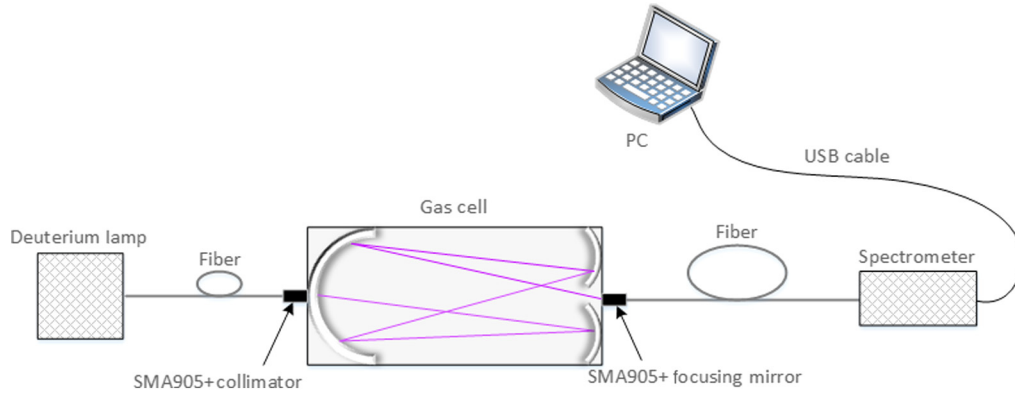


Fig. 4 The schematic diagram of the UV-DOAS detection system.

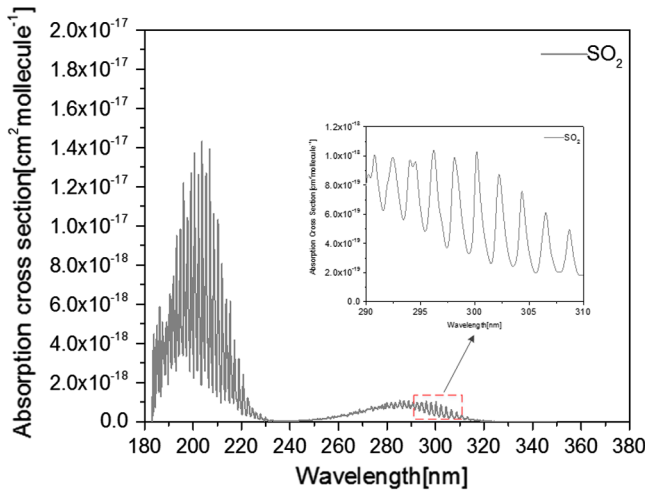


Fig. 5 The absorption spectrum of SO<sub>2</sub> in 190 to 310 nm.

shunted by effective measures. The intensity of the fluorescence signal,  $I_f$ , is proportional to the intensity of the light absorbed by the molecule:

$$I_f = \psi(I_0 - I), \quad (1)$$

where  $I_0$  is the input light intensity,  $I$  is the output light intensity, and  $\psi$  is a constant that is determined using the fluorescence quantum efficiency.

According to the Lambert–Beer law, the relationship between  $I_f$  and the medium concentration can be established as follows:

$$\begin{aligned} I_f &= \psi I_0 (1 - 10^{-\epsilon lc}) \\ &= \psi I_0 \left[ 2.3\epsilon lc - \dots \frac{(-2.3\epsilon lc)^n}{n!} - \dots \right] \\ &= 2.3\psi \epsilon lc I_0 (\epsilon lc < 0.05), \end{aligned} \quad (2)$$

where  $c$  is the medium concentration,  $\epsilon$  is the gas molecule molar absorption coefficient, and  $\epsilon lc$  is absorbance.

When  $I_0$  is constant, Eq. (2) can be expressed as

$$I_f = Kc. \quad (3)$$

The gas concentration can be quantified by measuring the fluorescence intensity. UV fluorescence spectroscopy is more sensitive than UV-DOAS because it measures the fluorescence intensity superimposed on a very small background and it has favorable selectivity. However, not all substances fluoresce under certain conditions, indicating that the application range of UV fluorescence spectroscopy is narrower than that of UV-DOAS.

Among the decomposition products of SF<sub>6</sub>, SO<sub>2</sub> has been the focus of many UV fluorescence detection studies. Pulsed fluorescence monitoring of SO<sub>2</sub> based on the UV fluorescence principle has become the standard method in many

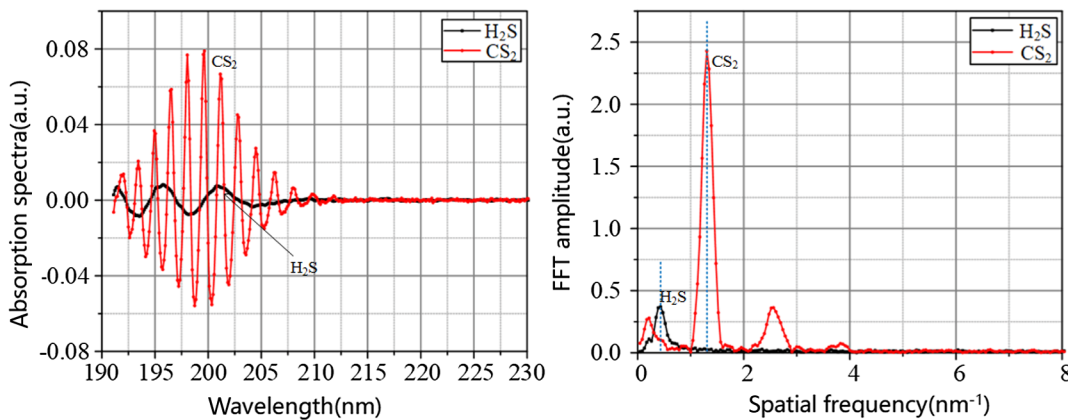


Fig. 6 Wavenumber-domain curves of CS<sub>2</sub> and H<sub>2</sub>S. The absorption of CS<sub>2</sub> in the wave number domain will not be affected, its concentration can be determined.

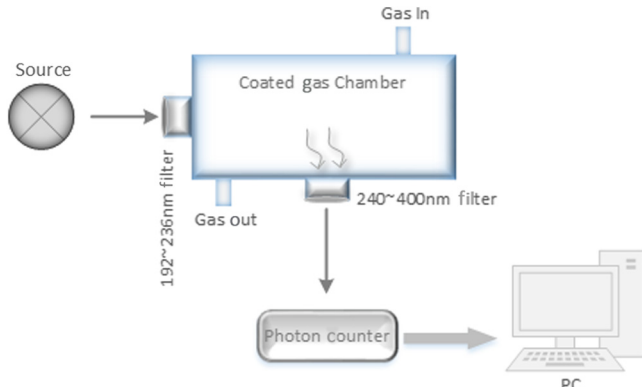


Fig. 7 The structure of UV fluorescence detection device.

countries, for the World Health Organization, and in global testing systems. UV fluorescence detection devices for SO<sub>2</sub>, such as Model T100 (Teledyne-API), 43i-TLE (Thermo Electron Corporation), and SERINUS 50 (Ecotech), have been commercialized and mainly used for environmental monitoring. These devices can achieve a detection limit of the order of ppb. However, UV fluorescence detection devices are relatively expensive. Moreover, the background gas in the SF<sub>6</sub>-insulated electrical equipment is different from that in air monitoring. Zhou et al.<sup>39</sup> reported a UV fluorescence detection device for SF<sub>6</sub> decomposition products, as shown in Fig. 7. A deep-UV deuterium lamp with an output range of 190– to 00 nm was used as the light source. The input to the gas cell was supplied through a filter with a range of 192 to 236 nm. Fluorescence detection was performed at 90 deg with respect to the excitation beam to avoid the strong radiation of the excitation light. At the output, a filter with a range of 240 to 400 nm was employed to exclude scattering interference from the excitation light. A photomultiplier tube is used for detection. The entire device was placed in a self-designed dark box to reduce external interference. The inside of the gas cell was coated with Teflon, and the connector was made of stainless steel and Teflon tubing to prevent SO<sub>2</sub> adsorption. The detection limit of the device was 110.94 ppb with SNR = 3 in the background gas of SF<sub>6</sub>. The background signals were not affected by changes of temperature and pressure, whereas the SO<sub>2</sub> fluorescence signals show a strong growth trend with the increase of temperature and pressure.

The structure of this device is simple and compact. The optical path of the gas chamber is 0.2 m, and its volume is 360 mL. The commercial light source and detector are miniaturized and integrated. Therefore, a portable or handheld device can be developed on the basis of this structural scheme.

### 3 Infrared Spectroscopy

#### 3.1 Fourier Transform Infrared Spectrometry

An FTIR spectrometer is a preferred research instrument due to the high SNR, high resolution, accurate wavelength, favorable repeatability, and stability provided by it.<sup>40</sup> FTIR has numerous applications in many fields. The detection of SF<sub>6</sub> decomposition products using FTIR technology can be traced back to the 1990s. Piemontesi et al.<sup>41</sup> studied the effect of H<sub>2</sub>O and O<sub>2</sub> on the decomposition products

of SF<sub>6</sub> using FTIR. They detected the products S<sub>2</sub>F<sub>10</sub>, SOF<sub>2</sub>, SOF<sub>4</sub>, CF<sub>4</sub>, HF, and CO and discovered that the presence of H<sub>2</sub>O and O<sub>2</sub> helped reduce the S<sub>2</sub>F<sub>10</sub> content. Pilzecker et al.<sup>42</sup> analyzed the characteristics of the colorimetric tube, ion mobility spectrometry, and FTIR in studying the decomposition products of SF<sub>6</sub>. Ion mobility spectrometry and FTIR showed strong correlation in SOF<sub>2</sub> detection. The detection limit of ion mobility spectrometry was found to be 40 ppm. Compared with the other two methods, the colorimetric tube had a lower detection limit and had difficulty detecting SO<sub>2</sub> and HF. Ding et al.<sup>43</sup> used FTIR to analyze the adsorption of SF<sub>6</sub> and its decomposition products by employing carbon nanotube sensors, and they proposed a new method for detecting SF<sub>6</sub> decomposition products. IEC60480<sup>44</sup> specifies the test standard for the detection of SF<sub>6</sub> decomposition products using FTIR.

Zhang et al.<sup>45–50</sup> conducted a series of FTIR studies on the decomposition products of SF<sub>6</sub>. The studies were based on the principle of White-Cell. They designed a gas cell with a 20-m-long path length, which was matched with FTIR. By comparing the results obtained using the FTIR equipped with this gas cell with those obtained using GC, the FTIR was found to detect a greater number of products than the gas chromatograph. The typical wave numbers of the absorption of SF<sub>6</sub> and its decomposition products in the IR band were obtained, as listed in Table 2. In addition, Zhang et al. used two-dimensional correlation spectroscopy to magnify the spectrum so that SF<sub>6</sub> decomposition products such as SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub>, SF<sub>4</sub>, SOF<sub>4</sub>, CO, SO<sub>2</sub>, and CF<sub>4</sub> could be detected under the background of SF<sub>6</sub>, which successfully solved a problem: that the information of other products is submerged owing to the strong absorption peak of SF<sub>6</sub>. Zhang et al. conducted numerous studies on the mechanism of SF<sub>6</sub> decomposition under different discharge conditions, including changes in the types of decomposition products and in the gas production rates of different products. They made important contributions to the theory, which is based on SF<sub>6</sub> decomposition product analysis to determine insulation faults in equipment.

Although FTIR can be used for on-line monitoring,<sup>24,25</sup> there exists no commercial FTIR spectrometer for the on-line monitoring of SF<sub>6</sub> decomposition products. The gas

Table 2 Typical absorption peaks of SF<sub>6</sub> decomposition products.

Type	Wavenumber (cm <sup>-1</sup> )	Wavelength (μm)
SO <sub>2</sub> F <sub>2</sub>	539/544/552	18.6/18.4/18.1
SOF <sub>2</sub>	530/1330/1340	18.9/7.52/7.46
CF <sub>4</sub>	1283	7.79
SO <sub>2</sub>	1169/1360	8.55/7.35
H <sub>2</sub> S	2625	3.81
HF	3644	2.74
SF <sub>4</sub>	746	13.4
SOF <sub>4</sub>	752	13.3
SF <sub>6</sub>	610/946/1270/1595/1720	16.4/10.6/7.9/6.27/5.81

cell and quantitative algorithm must be customized if FTIR has to be used for on-line monitoring. FTIR is primarily used in the laboratory for analysis. With the long-path gas cell, detecting almost all the SF<sub>6</sub> decomposition products is possible. The usual practice involves performing a preliminary detection of the products in the equipment through the portable or on-line detection device. If abnormal gases are found, the internal gas of the equipment can be sampled. Detailed analysis can be then performed in the laboratory using FTIR.

### 3.2 Photoacoustic Spectroscopy

PAS is an indirect spectroscopic method that combines the theory of IR absorption spectroscopy with the photoacoustic (PA) effect. The concentration of a gas can be calculated by measuring the intensity of the acoustic signal excited by the PA effect. When the excited electrons return to the ground state, energy is released outward in two ways: radiation and nonradiative transitions, where the nonradiative transition releases heat and changes the ambient pressure. If the incident light is modulated and injected into the gas cell at a certain frequency, a periodic heat source is formed that changes the pressure periodically, resulting in the generation of an acoustic signal. The gas concentration can be calculated indirectly by detecting the acoustic signal. This is the basic principle of PAS, as shown in Fig. 8.

PAS has many advantages over traditional absorption spectroscopy:

1. The strength of PA signals is related to the light energy absorbed by gas molecules. If there is no absorption, there is no PA signal, so it is a background-less technology.
2. The light intensity detector in traditional absorption spectrometers is wavelength-dependent, whereas the detector used in a PAS is wavelength-independent.
3. PAS offers good stability and high sensitivity. By using a laser light source and high-sensitivity microphones, theoretical detection limits of the order of ppb can be achieved;<sup>51,52</sup>
4. PAS detection system is smaller, has fast response, and is easy to monitor on site.

Based on these advantages, PAS has received widespread attention. A few studies have reviewed the research on the use of PAS for gas detection. Elia et al.<sup>53</sup> introduced PAS gas-sensing technology based on semiconductor laser sources. An IR tunable semiconductor laser was considered an ideal light source for gas detection, and it has been used widely in environmental monitoring, chemical detection,

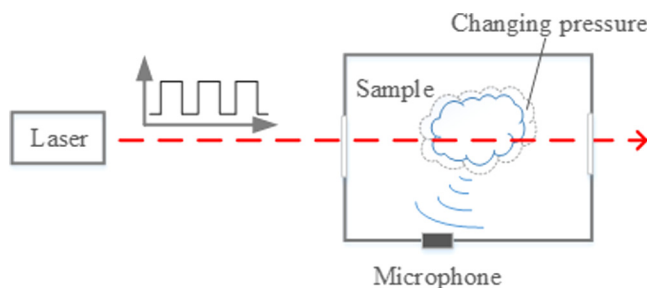


Fig. 8 The principle of PAS.

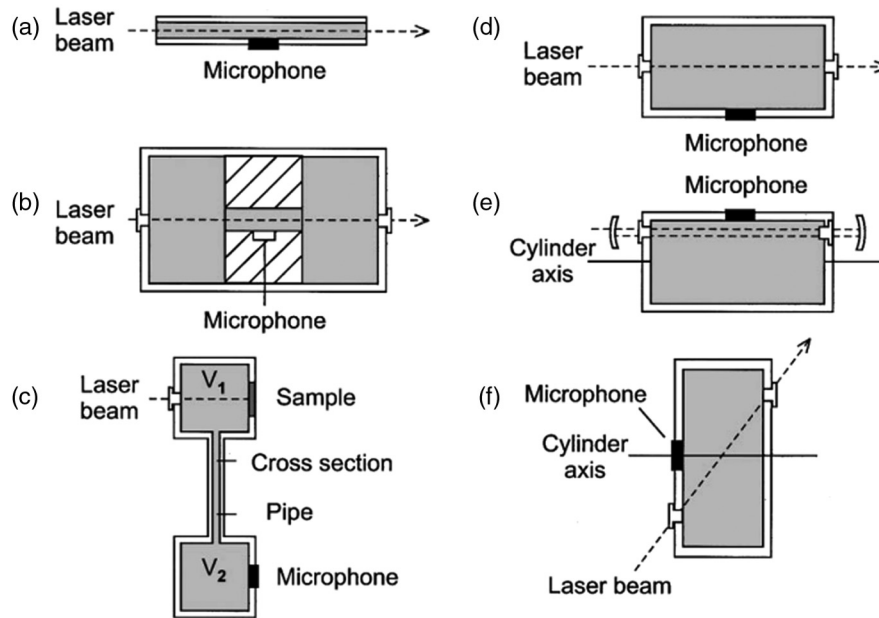
industrial emission monitoring, and other fields. In addition, the standard PAS and differential PAS methods were summarized, and quartz-enhanced PAS was discussed. Pogány<sup>54</sup> introduced the development of PAS and discussed the special problems associated with PAS in practical applications, including the problems of noise and spectral interference. Pogány summarized the practical applications of PAS, including in environmental monitoring and industrial fields, and outlined prospects for the development of PAS. Miklos<sup>55</sup> described three types of PA cells used in PAS—the one-dimensional acoustic resonator [Figs. 9(a) and 9(b)], Helmholtz resonator [Figs. 9(c)], and cavity resonator [Figs. 9(d)–9(f)]—and discussed their application in gas detection.

PAS can be used to detect SF<sub>6</sub> decomposition products with absorption characteristics in the IR region. Lin et al.<sup>56</sup> developed a PAS device for detecting SF<sub>6</sub> decomposition products, as shown in Fig. 10. The device employed broadband IR light as the light source, a highly sensitive electret microphone for sound signal detection, and a mechanical chopper for light modulation, and the device could detect SO<sub>2</sub>F<sub>2</sub>, SO<sub>2</sub>, CF<sub>4</sub>, and CO<sub>2</sub> with detection precision of 0.831, 1.888, 2.213, and 5.695 μV/ppm, respectively. Qiu et al.<sup>57</sup> used a broadband IR source with a wavelength of 0.6 to 25 μm to obtain a PAS device for detecting SOF<sub>2</sub>. A chopper was employed for modulation. To avoid the influence of the absorption of other products, a filter with a range of 7440 ± 20 nm was used. The longitudinal resonant PA cell was made of pure copper, and both ends were sealed with ZnSe. The measured quality factor of the cell was 47. The detection limit of the device was 4.6 ppm, and the average error was 5.9%. According to Qiu et al., PAS is a reliable method for the on-line monitoring of SF<sub>6</sub>-insulated electrical equipment.

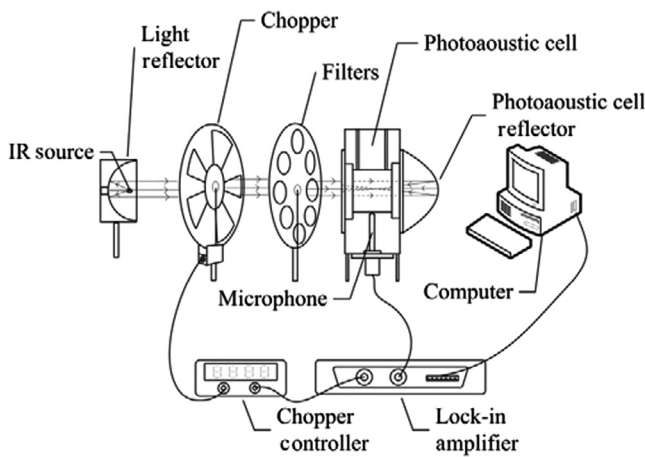
The performance of PAS can be further enhanced by improving their components. Wu et al.<sup>58</sup> used a customized quartz tuning fork as a microphone and amplified light power using an erbium-doped fiber amplifier. They developed a PAS sensor for detecting H<sub>2</sub>S, and the detection limit of this sensor was 890 ppb. Varga et al.<sup>59</sup> developed a two-channel H<sub>2</sub>S on-line monitoring system with a detection limit of 0.5 ppm, which was suitable for the natural gas industry. Laboratory and field tests showed that this system could perform long-term and stable monitoring in harsh industrial environments.

The use of an interferometric cantilever sensor instead of a conventional microphone can enhance the sensitivity by at least one order of magnitude.<sup>60</sup> Gasera Ltd. had developed various PA detectors based on the interferometric cantilever.<sup>61,62</sup> The working principle of the cantilever-enhanced PA cell is shown in Fig. 11. Interaction between the gas in the cell and the modulating light leads to changes in pressure. The changing pressure causes the cantilever to vibrate. A Michelson interferometer is employed to optically measure the displacement of the free end of the cantilever and thus acquire a PA signal.

Zhang et al.<sup>63</sup> analyzed the decomposition of SF<sub>6</sub> and its reaction with other impurities to form H<sub>2</sub>S using Materials Studio. They then employed a cantilever-enhanced PAS to detect H<sub>2</sub>S. The PA cell and microsilicon cantilever microphone system were manufactured by Gasera Ltd. A distributed feedback laser diode with a center wavelength of



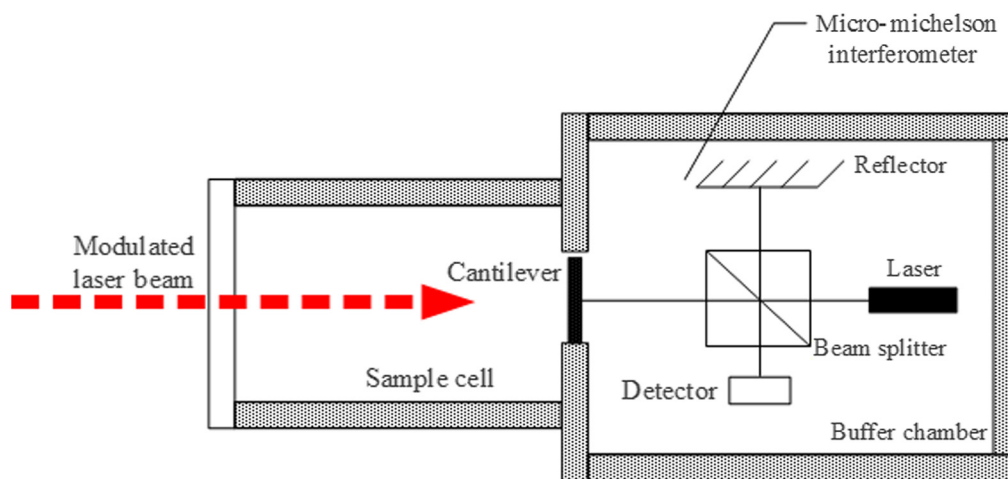
**Fig. 9** Different types of PA cells. The figure comes from Miklos.<sup>55</sup> The (a, b) one-dimensional acoustic resonator, (c) the Helmholtz resonator, and (d–f) the cavity resonator.



**Fig. 10** The structure of PAS device. The figure reproduced from Ref. 56.

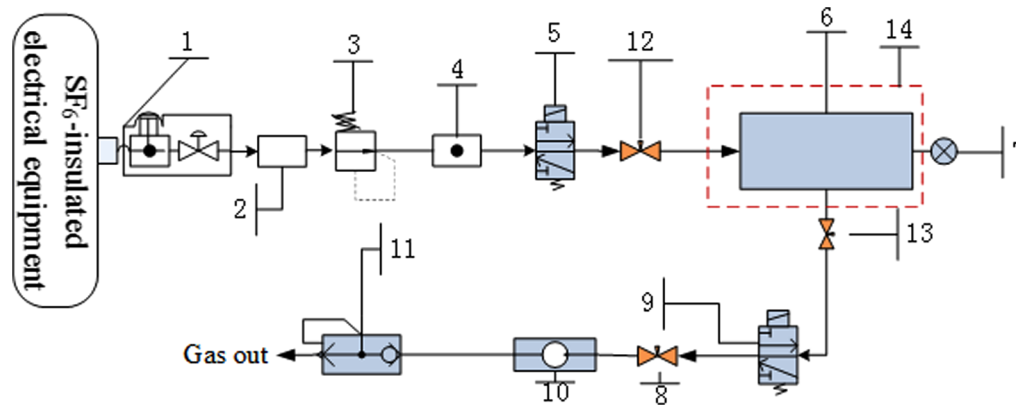
1577.86 nm was adopted in the study. The results show that under two background gases, N<sub>2</sub> and SF<sub>6</sub>, the detection limit was 0.84 and 1.75 ppm, respectively. Zhang et al.<sup>63</sup> analyzed the factors that influence cantilever-enhanced PAS gas detection and found that the change in the PA signal amplitude decreases with an increase in the pressure or temperature of the PA cell. They also found that the detection platform is more sensitive to pressure than temperature.

The on-line monitoring PAS system has a few commercial applications. It has promising applications for SF<sub>6</sub>-insulated electrical equipment. After the target gas and corresponding light source are determined, an on-line monitoring device with a PA cell can be developed for SF<sub>6</sub> decomposition products. A feasible scheme of on-line monitoring PAS for SF<sub>6</sub>-insulated equipment is shown in Fig. 12. Because the pressure in the equipment is several times higher than atmospheric pressure, a pressure reducing valve is installed in



**Fig. 11** The principle of the cantilever-enhanced PA cell. Sample cell and micro-Michelson interferometer.





**Fig. 12** The schematic diagram of on-line monitoring PAS for the SF<sub>6</sub>-insulated electrical equipment. (1) Sampling port, (2) metal dust filter, (3) pressure reducing valve, (4) three-way valve, (5) switch valve, (6) PAS device, (7) pressure sensor, (8) restriction valve, (9) switch valve, (10) vacuum pump, (11) check valve, (12, 13) flow control valve, and (14) passive vibration isolation device.

the gas path. A three-way valve is used to introduce pure and dry N<sub>2</sub> to clean the PA cell.

#### 4 Technology for Detecting SF<sub>6</sub> Decomposition Products

With the development of optical detection technology, researchers are pursuing higher detection accuracy, higher sensitivity, and faster detection time. Equally, it is hoped that the structure would be as simple and compact as possible for onsite or on-line monitoring. Thus, many optical technologies are continuing to emerge. The following are two technologies that can be used for detecting SF<sub>6</sub> decomposition products.

##### 4.1 Cavity Ring-Down Spectroscopy

CRDS is a direct absorption technique that can be performed with pulsed or continuous light sources. A significantly higher sensitivity can be obtained with CRDS than with conventional absorption spectroscopy. CRDS was formally proposed by O'Keefe and Deacon in 1988.<sup>64</sup> CRDS uses the ring-down time to invert the gas concentration, which reduces the impact of light source fluctuation on the detection results. In addition, light can be reflected back and forth multiple times in the ring-down cavity, which can extremely improve the gas absorption path.

Pulse CRDS (P-CRDS) is used as an example. Its working principle is shown in Fig. 13. The detection system consists of a pulsed laser source, a ring-down cavity composed of two high-reflectance mirrors (>99.9% reflectance), a photodetector, and other products. The pulsed laser is coupled with the ring-down cavity, and light is reflected multiple times in the ring-down cavity. During each reflection, the laser interacts with the target gas while some weak light is transmitted. According to the Lambert–Beer law, the transmitted light signal decays exponentially. The ring-down time  $\tau$  is the time required for the light intensity to decay to  $1/e$  of the initial light intensity. The change in the ring-down time  $\tau$  reflects the system loss, including intrinsic losses and gas absorption losses. The intrinsic system losses, such as connector loss and fiber loss, are constant. Therefore, the gas absorption loss can be determined by the change in the ring-down time  $\tau$ , and then, the gas concentration can be calculated. For example, when the ring-down time

decreases, the gas absorption loss increases and the gas concentration thus increases.

CRDS has strong anti-interference ability and high detection accuracy, and it is suitable for trace gas detection. Several scholars have used it to detect SF<sub>6</sub> decomposition products. Zhang et al.<sup>65</sup> adopted a modular design method based on CRDS to design an on-line system for monitoring SF<sub>6</sub> decomposition products, and the feasibility of this system for detecting SF<sub>6</sub> decomposition products was demonstrated.

However, the limitation of CRDS lies in its dependence on ultrahigh-reflectivity mirrors. In actual measurements, if the mirror reflectance decreases owing to mirror pollution or ring-down cavity vibration, the measurement error is dramatically increased. Furthermore, pattern matching of the cavity is a problem. To solve these problems, a new type of CRDS technology is introduced herein: fiber loop ring-down spectroscopy (FLRDS).<sup>66–69</sup>

FLRDS is based on CRDS. An optical fiber is used to replace the ring-down cavity, and this fiber directs the pulsed light to circulate in the fiber loop. The basic principle of FLRDS is shown in Fig. 14. The equipment is composed of two  $2 \times 1$  couplers and a gas cell. Pulsed light enters the fiber ring cavity through coupler C1 to circulate, and during each cycle, the light interacts with the gas in the cell. A small percentage of the light enters the photodetector through coupler C2, but most of the light continues to circulate in the fiber ring cavity, and this continues until the light is completely attenuated.

All-fiber connections are employed in FLRDS. Forming a fiber sensor network for the on-line monitoring of trace gas is easy.<sup>70</sup> However, the detection precision of FLRDS cannot currently meet the requirement of SF<sub>6</sub> decomposition products.<sup>68,71,72</sup> Thus, further detailed research is required.

##### 4.2 Photonic Crystal Fibers

A PCF, also called a microstructured fiber, is shown in Fig. 15. The interior of such a fiber can be an air-core structure that allows for the transmission of photons within the air core.<sup>73</sup> This enhances the interaction of light and air, resulting in higher excitation efficiency and smaller losses. It is possible to create cells with long absorption paths.

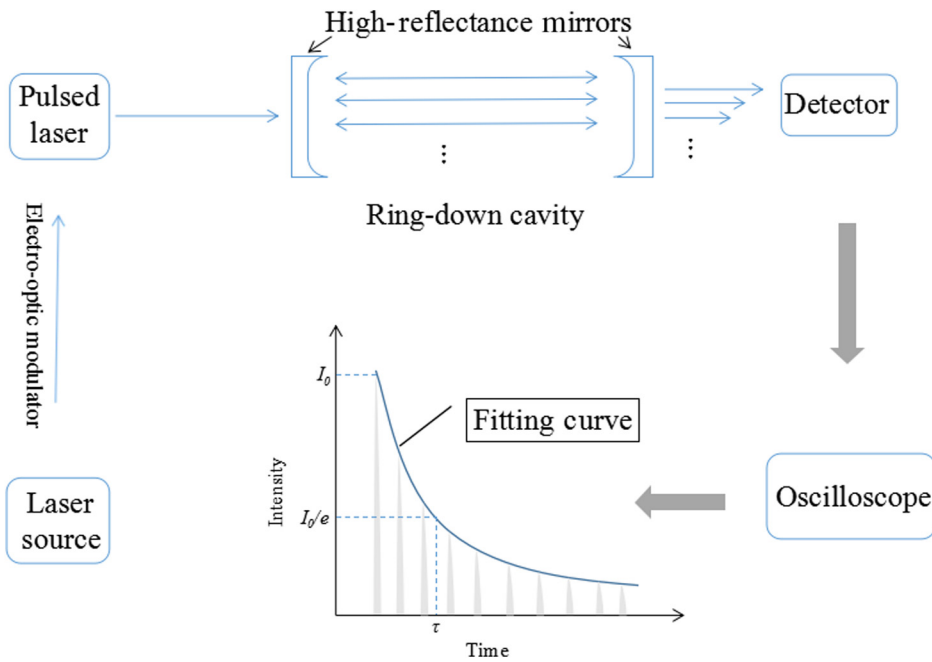


Fig. 13 The principle of CRDS.

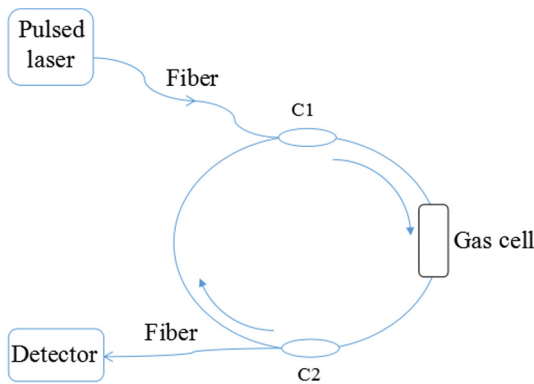


Fig. 14 The basic principle of FLRDS.

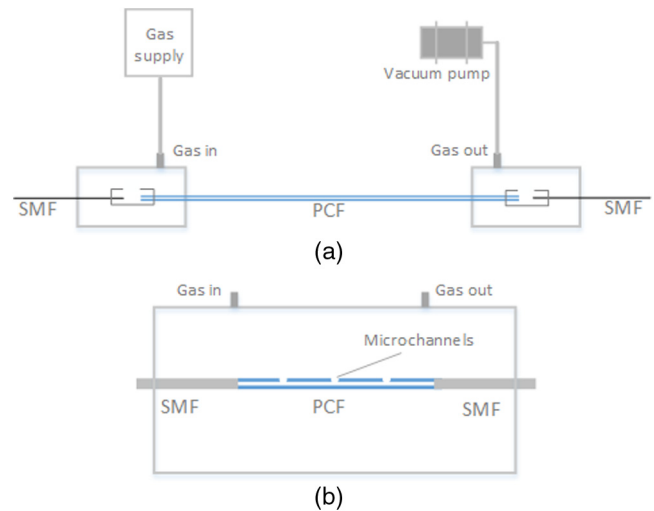


Fig. 16 Two ways to make the gas enter into the cell. (a) Using micro-gap and (b) drilling microchannels.

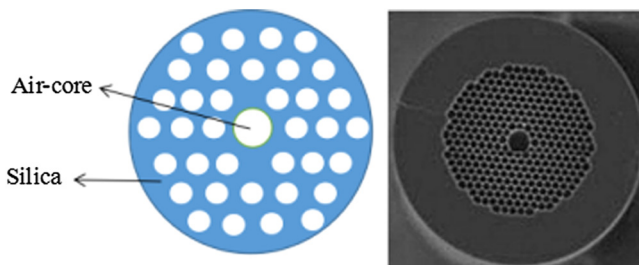


Fig. 15 The structure of PCF.

However, it is necessary to consider how to input the gas into the cell. There are generally two ways to achieve this: to create a small gap between the PCF and the input/output of the optical fiber to allow gas to flow in; and to use a femtosecond laser to drill holes in the side of the PCF, which enables accelerated inflow of gas, as shown in Fig. 16.

Li et al.<sup>74</sup> chose to create a gap of 10  $\mu\text{m}$  between the PCF and the input/output of the fibers. They evacuated the gap for

12 h after cleaning it with N<sub>2</sub>. Then, the target gas flowed into the PCF cell under a pressure of 100 kpa. The results showed that the transmission loss of CH<sub>4</sub> at concentrations of 0.5% to 4% tended to stabilize after 6 min; the transmission fluctuation for C<sub>2</sub>H<sub>6</sub> with 10% concentration was 0.2 dB in the first 2000 s. Jin et al.<sup>75</sup> used a femtosecond laser to drill the side of a 0.62-m-long PCF, and the total loss after drilling was 4 dB. In addition, they used an all-fiber photothermal spectroscope with the PCF to detect C<sub>2</sub>H<sub>2</sub>, obtaining a detection limit of 30 ppb. Lehmann et al.<sup>76</sup> indicated the characteristics of different modes of gas diffusion: a PCF microgap required the use of a vacuum pump or pressurization to inject gas, and the gas diffusion time was longer. Moreover, fabricating the PCF cell by means of femtosecond laser side-drilling was complicated,

**Table 3** Several optical detection methods for SF<sub>6</sub> decomposition products.

Method	Types						Application	Cost	Sensitivity	Speed
	SO <sub>2</sub>	H <sub>2</sub> S	CS <sub>2</sub>	SOF <sub>2</sub>	SO <sub>2</sub> F <sub>2</sub>	CF <sub>4</sub>				
UV-DOAS	✓	✓	✓				Portable	Medium	Sub-ppm	Fast
UV fluorescence	✓						Portable or handheld	Low	Sub-ppm	Fast
FTIR (with 20 m gas cell)	✓	✓		✓	✓	✓	Laboratory or on-line monitoring	High	ppm	Medium
PAS	✓	✓		✓	✓	✓	On-line monitoring	High	Sub-ppm	Fast

and there was a risk of destroying the PCF structure during the drilling process.

Gas detection with PCFs has extremely high precision. However, the production process of the gas cell is complicated. The gas cell may achieve popularity for commercial applications in the future. Thus, we can continue to pay attention to the developments in this field.

## 5 Conclusion

The various advantages of the optical detection method, such as high precision and speed, portability, on-line monitoring, and nondestructive measurement, enable it to have good application prospects in the power industry. Different methods have different application scenarios, and their cost, detection technique, and sensitivity also vary. Table 3 summarizes the detection methods mentioned herein. Because CRDS and PCF have few applications in the detection of SF<sub>6</sub> decomposition products, they are not listed in the table.

The detection devices based on UV-DOAS and UV fluorescence can conveniently sample and detect SF<sub>6</sub> decomposition products on-site. The UV fluorescence device can also be modified into a handheld device, which can reduce the work intensity of on-site inspection personnel. The detection devices based on UV-DOAS and UV fluorescence have a fast response. Moreover, the cost of the UV-DOAS and UV fluorescence devices is lower than that of FTIR and PAS. However, few products can be detected with the UV-DOAS and UV fluorescence devices. FTIR can be used to detect almost all products. Although it can be used for on-line monitoring, the operation process for multiproduct measurement is complicated. The operators must be trained accordingly. Its response speed is related to the spectral resolution. A long time is required to perform a fine-resolution analysis. Therefore, analyzing the sample gas in the laboratory through FTIR is the most suitable option. PAS, the most suitable method for on-line monitoring, can be used to detect multiple products with a corresponding light source or filter. However, PAS is costlier than the UV-DOAS and UV fluorescence devices.

In summary, for the consumer and junction substations, on-line monitoring PAS can be used to ensure real-time access to the insulation. The UV-DOAS and UV fluorescence devices are cheap and easy to use. These devices can be used in the routine maintenance of equipment. The UV-DOAS and UV fluorescence devices can detect limited components. However, when an abnormal gas is detected, it can be removed from the equipment for FTIR detection to quantitatively analyze the products in detail. By combining

various optical detection methods, the detection accuracy of SF<sub>6</sub> decomposition products can be ensured. Thus, the types and severity of insulation defects can be determined in an effective and a timely manner.

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