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# Fourier-transform infrared spectroscopy for quantification of hydrogen fluoride in sulfur hexafluoride decomposed by partial discharges and sparks

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# Abstract

Hydrogen fluoride has been measured by infrared spectroscopy after SF<sub>6</sub> decomposition by either electric partial discharges or sparking. Reference standard spectra necessary for quantification were calculated using the HITRAN96 data base. It is shown that the pressure broadening functions as tabulated for atmospheric conditions, are also applicable for SF<sub>6</sub> as matrix gas. Since a strong *J*-quantum number dependence exists for pressure broadening of the individual HF-lines, the folding effects for the spectra based on a sinc<sup>2</sup>-instrumental line shape function of the FT-IR-spectrometer as used in this study lead to significantly different line dependence of the trace volume mixing ratio was studied for a spectral resolution of  $0.5 \text{ cm}^{-1}$ , which is much larger than the true line halfwidths found for an SF<sub>6</sub> pressure close to 100 kPa. Quantitative results are reported for spectra obtained at optical pathlength of 10 cm and partial HF pressures up to 40 Pa using least-squares fitting and several HITRAN96derived standard spectra. Furthermore, results from multivariate partial least-squares calibration are presented with a standard error of prediction of 0.2 Pa.

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## 1. Introduction

Mid-infrared spectroscopy has often been used for trace gas analysis due to its analytical multicomponent capability [1]. Hydrogen fluoride is a special gas which has recently received a lot of attention. For example, it is formed during suppression of fires by halon and replacement agents [2,3], and it is the main gas of interest in emission monitoring of waste incinerators [4], and aluminium smelter plants [5]. Other studies were carried out with regard to SF<sub>6</sub> decomposition within gas-insulated high-voltage equipment, where HF is also found as a short-lived toxic and corrosive by-product [6,7]. Besides the use of near-infrared diode-lasers, Fourier-transform infrared spectrometers are often employed for quantitative measurements. However, the linearity range of the maximum line absorbances in dependence of the trace volume mixing ratio can suffer from an insufficient spectral resolution—a

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maximum of  $0.5 \text{ cm}^{-1}$  has frequently been used for gas analysis compared to the significantly smaller line halfwidths at atmospheric pressure.

Standard reference spectra can be calculated based on the HITRAN96 data base [8]. It will be shown that the pressure broadening functions as tabulated for atmospheric conditions, are also applicable for SF<sub>6</sub> as matrix gas. Due to a strong J-quantum number dependence for the pressure broadening of the individual HF-lines, the folding effects for the spectra based on the instrumental line shape function of an FT-IR-spectrometer lead to significantly different individual line dependent deviations from the desired simple linear Beer law approach. Multivariate classical least-squares and partial least-squares approaches have been used in this study for quantification, and results will be reported for spectra of samples obtained from SF<sub>6</sub> within a discharge chamber under the main influence of electric partial discharges.

## 2. Experimental

The decomposition of  $SF_6$  by partial discharges and sparking was studied under a pressure between 200 and 300 kPa, which was provided for insulation inside a discharge chamber constructed from stainless steel and teflon® using different point/plane configurations. The point electrode was a needle made from stainless steel, whereas the plane electrode material was either silver, aluminium, tungsten, tungsten/copper alloy or copper for discharge experiments. For sparks pins of the latter material were used instead of the needle; for more details, see Ref. [7].

The spectra of the SF<sub>6</sub> decomposition products were recorded by an FT-IR-spectrometer model IFS 113v from Bruker Optik (Ettlingen, Germany) equipped with a KBr-beamsplitter and a mercury cadmium telluride (MCT) detector (cut-off at 530 cm<sup>-1</sup>) operated at liquid nitrogen temperature. The stressed SF<sub>6</sub> gas from the discharge chamber was directly expanded into a heatable cell of 10 cm optical pathlength (cell body from stainless steel) delivered by SPECAC (Orpington, UK) with an average cell pressure of 73.5 kPa. Within our study, infrared spectra were recorded by co-adding 100 interferograms at a spectral resolution of  $0.5 \text{ cm}^{-1}$ . For spectrum calculation (with zero-fill factor of eight and triangular apodization), the option of the Bruker OPUS software for correction of the MCT detector non-linearity effects was used.

Quantification was done using classical least squares (CLS) with four different HF partial-pressure (10, 20, 30 and 40 Pa, respectively) adjusted spectral data from HITRAN96, including sinc<sup>2</sup>-instrumental line shape (ILS) convolution (equivalent to triangular apodization of the interferograms) [8], application of a wavenumber-proportional shift in the wavenumber axis for the spectral range of  $4300-3500 \text{ cm}^{-1}$  (for the lower limit the shift was  $-0.03 \text{ cm}^{-1}$ ) and baseline correction. The number of sample spectra was 34 (partial HF pressure values were between zero and 42 Pa, standard deviation for the sample population 12.4 Pa and mean value was 8.8 Pa). The CLS spectrum evaluation with consideration of HF and H<sub>2</sub>O was based on our PC-software package programmed in MATLAB (The Mathworks, South Natick, MA, USA) and on calculations based on GRAMS32 from Thermo Galactic (Salem, NH, USA). The CLS results were used later as input for multivariate partial least squares (PLS) calibrations. Multivariate PLS calibration including cross-validation using the same spectrum interval and our special spectral variable selection procedure was carried out using a PC-software package programmed in MATLAB by ourselves.

### 3. Results and discussion

The HF produced under electrical stress from SF<sub>6</sub> decomposition, for which the largest concentrations were obtained under partial discharge conditions, can be reliably quantified using the rotation-vibration lines of its fundamental stretching vibration band around 4000 cm<sup>-1</sup>. A spectrum, which was measured from a contaminated SF<sub>6</sub> sample within our discharge chamber, is shown in the upper trace of Fig. 1A, whereas the lower spectrum of water vapour was obtained from a sample with significant humidity after chamber leakage. The spectral range is free of absorption bands from other contaminants or the SF<sub>6</sub>-matrix.

The quantitative evaluation of the gas spectra needs reference spectra, which can be calculated from HITRAN96 data, compiled for pressure broadening of





Fig. 1. (A) IR-spectrum of HF in SF<sub>6</sub> (top, after decomposition by sparks, optical pathlength 10 cm, total pressure 86.6 kPa; the H<sub>2</sub>O spectrum below from an experiment with discharge chamber leakage) (B) Spectrum of HF in air, calculated for 100 ppm<sub>v</sub>, atmospheric pressure 101.3 kPa, L = 10 cm; (C) result after ILS convolution, spectral resolution = 0.5 cm<sup>-1</sup>, triangular apodisation (upper trace), spectral residue from scaled absorbance subtraction (see text).

HF-lines under atmospheric conditions; see also Ref. [9]. For our situation, however, the matrix gas is  $SF_6$  instead of air, so that intensive literature searching was carried out for line broadening parameters obtained for a number of different matrix gases [10]. A paper on the calculation of self- and foreign-gas broadened linewidths for  $SF_6$  based on the Anderson–Tsao–Curnutte theory (matrix gases were He, Ar, O<sub>2</sub>, N<sub>2</sub>, HF and  $SF_6$ ) was provided by Tejwani and Fox [11], which lists molecular and atomic parameters needed for the theoretical modelling of collision processes. The broadening parameters for the P(8) line of the fundamental band of DF at 3.4 µm for

various matrix gases have been determined by Bonczyk [12]. For  $N_2$  and  $SF_6$  the foreign-gas broadening was found to be equal. In this context also a study by Crane–Robinson and Thompson [13] is of interest whereby the pressure broadening for CO in the fundamental band was investigated. The foreign-gas broadening of 23 different matrix gases was studied with similar results for  $N_2$  and  $SF_6$ .

With these literature results we decided to use to HITRAN96 data base also for our HF-reference spectrum calculation. An HF spectrum calculated for a matrix of air at a pressure of 101.3 kPa, a volume ratio of 100  $ppm_v$  (equivalent to a partial pressure of 10 Pa) and an optical pathlength of 10 cm is shown in Fig 1B. Furthermore, the same spectrum had been folded with a sinc<sup>2</sup> ILS for a nominal spectral resolution of  $0.5 \text{ cm}^{-1}$  which is presented in Fig 1C (upper trace). The lower trace spectrum is the spectral residual from the subtraction of an absorbance spectrum calculated for 400 ppm<sub>v</sub> of HF minus the scaled reference obtained for 100  $ppm_v$  (the scaling factor was obtained by minimising the residues within the whole interval shown by least squares). Three examples of the significant variation in J-quantum number dependent air-broadening together with the convolution results are given in Fig. 2. As principally a slight deviation - in addition to a J-quantum number dependent variation - is expected to exist for HF-line broadening by air and SF<sub>6</sub>, respectively, the total pressure was varied for the line broadening effects simulated by an atmospheric matrix gas within our spectral calculations. The maximum line intensities versus different partial HF pressures, which were relevant for our SF<sub>6</sub>-decomposition monitoring, are presented in Fig. 3 for the same three *R*-branch lines of HF as shown in Fig. 2. The deviations from the desired linear Beer law behaviour are evident for the spectral resolution of  $0.5 \text{ cm}^{-1}$ .

Therefore, the CLS-evaluations were based on spectral reference data calculated for different HF partial pressures. In the first stage, the concentration estimate was obtained from a least squares fit using the reference spectrum of the lowest HF-volume mixing ratio (100 ppm<sub>v</sub>). In a second step, the reference spectrum used for least-squares fitting was chosen on the basis of maximum closeness to the previously determined mixing ratio. The spectral residues from such a least-squares fit are displayed

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Fig. 2. Folding effects for individual lines of HF, calculated for conditions as given in Fig. 1B and C (solid curves: true line shapes, dashed curves: results from  $sinc^2$ -convolution).



Fig. 3. Non-linearity of maximum intensities of individual lines of HF after ILS-folding, calculated for different pressure broadening conditions as given in the figure legend to account for an  $SF_6$  matrix (optical pathlength 10 cm; see also Fig. 2).



Fig. 4. Spectral residues obtained for experimental FT-IR-spectra of decomposed  $SF_6$ -samples by least squares fitting using a reference spectrum calculated with a HF partial pressure close to the experimental value: upper trace for a spectrum of a sample with 420 Pa of HF—see also inset for the respective simulated (offset), experimental line shape and CLS-spectral residue—(a), and lower trace for a sample of 118 Pa (b).

in Fig. 4 for two different sample spectra. The inset provides details on the HF line shape obtained theoretically and experimentally, the latter of which is slightly asymmetric even after correction of the detector non-linearity effects, and the residual after spectral subtraction.

Interestingly, a least-squares fit of a 400 ppm<sub>v</sub> standard spectrum with a spectrum from 100 ppm<sub>v</sub> HF led to a 7.4% relative deviation in partial pressure prediction when based on the whole spectral interval as given above. A least-squares fit of a single line, e.g. of R(2), produced an even lower value with 11 % relative deviation, which shows impressively the need for non-linear modelling and evaluation.

The CLS-results above were used as concentration input also for a PLS-calibration, exploiting the spectral range of  $4300-3500 \text{ cm}^{-1}$ . For the concentration range found for the discharge and spark experiments, a standard error of prediction (SEP) of 0.33 Pa was found for a PLS-rank of 2, modelling even some non-linear spectral effects. The SEP obtained with the three largest maxima of the R(1), R(2) and P(2)-lines and baseline points nearby was 0.24 Pa (optimal PLS-rank = 5). The scatter plot for leave-one-out cross-validated HF concentration values given as partial pressure using the latter optimum PLS calibration model versus the results

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Fig. 5. Scatter-plot for leave-one-out cross-validated HF concentrations using PLS-calibration versus reference data obtained from CLS-evaluation with several standard HITRAN96 spectra calculated for sample-close HF partial pressures including ILS-folding.

from the CLS evaluation using many reference standards is shown in Fig.5.

#### 4. Conclusions

The influence of the ILS-folding on intensities and shapes of lines in the fundamental rotation-vibration band of HF, with trace concentrations measured at room temperature and an optical pathlength of 10 cm, has been calculated for an air matrix around atmospheric pressure. The pressure broadening coefficients as tabulated for atmospheric conditions can be favourably taken into account also for an SF<sub>6</sub> matrix as illustrated by the individual line shapes and the whole line intensity pattern simulated and experimentally measured. The PLS-calibrations were able to model slight non-linearities as found for the given experimental spectroscopic conditions.

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