



CHANCE project

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Report on experimental validation of the transitions with ^{36}Cl standards and detection limit

DELIVERABLE (D5.2)

Work Package 5 - Task 5.1

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5. Appendix	Erreur ! Signet non défini.

Abstract

This work represents the D5.2 deliverable of the Work Package 5 - task 5.1 of the CHANCE project (Characterization of conditioned nuclear waste for its safe disposal in Europe).

Rotational–vibrational transitions of H^{36}Cl are experimentally verified in the near-infrared and mid-infrared wavelength regions using Fourier-transform infrared spectroscopy and a sample with elevated amount of H^{36}Cl . The measured data in the near-infrared is in agreement with the calculated line positions (D5.1). Finally, estimated detection limits are reviewed.

1. Introduction

The CHANCE project aims to address the specific issue of the characterization of conditioned radioactive waste. The characterization of fully or partly conditioned radioactive waste is a specific issue because unlike for raw waste, its characterization is more complex and therefore requires more advanced non-destructive techniques and methodologies.

The first objective of the CHANCE project is to establish at the European level a comprehensive understanding of current conditioned radioactive waste characterization and quality control schemes across the variety of different national radioactive waste management programmes, based on inputs from end-users members such as Waste Management Organizations and storage operators.

The second objective of CHANCE is to further develop, test and validate techniques already identified that will improve the characterization of conditioned radioactive waste, namely those that cannot easily be dealt with using conventional methods. Specifically, the work on conditioned radioactive waste characterization technology will focus on:

- Calorimetry as an innovative non-destructive technique to reduce uncertainties on the inventory of radionuclides;
- Muon Tomography to address the specific issue of non-destructive control of the content of large volume nuclear waste;
- Cavity Ring-Down Spectroscopy (CRDS) as an innovative technique to characterize outgassing of radioactive waste.

The present report focuses on activities from Work Package 5 related to the development of the CRDS for the detection of radioactive gases. Task 5.1 of WP5 aims to develop instrumentation for detection of H^{36}Cl with laser spectroscopy. This deliverable summarises the experimental work carried out to validate the rotational–vibrational transitions of H^{36}Cl , transitions that has never been measured previously. This work will advance development of instruments based on optical spectroscopy of gaseous H^{36}Cl since detailed spectroscopic information is crucial first step for this development. Optical spectroscopy methods are well suited for detection of different simple compounds in gas phase. They often provide means for affordable and portable instruments, which are well suited for emission monitoring in nuclear facilities and their decommission sites.

Fourier-transform infrared spectroscopy (FTIR) method was used to detect and characterize the fundamental and first overtone rotational–vibrational bands of H^{36}Cl . Fundamental band lies in the mid infrared part of the electromagnetic spectrum and first overtone band in the near infrared. The gaseous H^{36}Cl sample for the experiments was prepared from ^{36}Cl -enriched NaCl -solution.

The work carried out in this task yielded a peer-reviewed publication (see Larnimaa, S.; Vainio, M.; Ulvila, V., **Infrared spectroscopy of radioactive hydrogen chloride H^{36}Cl** , *Journal of Quantitative Spectroscopy and Radiative Transfer*, (277) 2022).

2. Experimental work

A Bruker IFS 120 HR FTIR-instrument was used for this work (Figure 1). The FTIR method is well-suited for the characterization of rotational–vibrational transition bands since the instruments typically allows measurement of full transition band at once. A Globar light source, Ge-on-KBr beam splitter, and liquid-nitrogen-cooled InSb detector. The raw spectrum is a result of processing 10 co-added double-sided interferograms using the Mertz method (Griffiths, J.A. de Haseth, 1986). A resolution of 0.02 cm^{-1} (600 MHz) was used. The experimental settings of the FTIR instrument are listed in Table 1 and Table 2. The FTIR sample cell was a long IR quartz cell (Suprasil 300; FireflySci Type 34) with a path length of 10 cm.

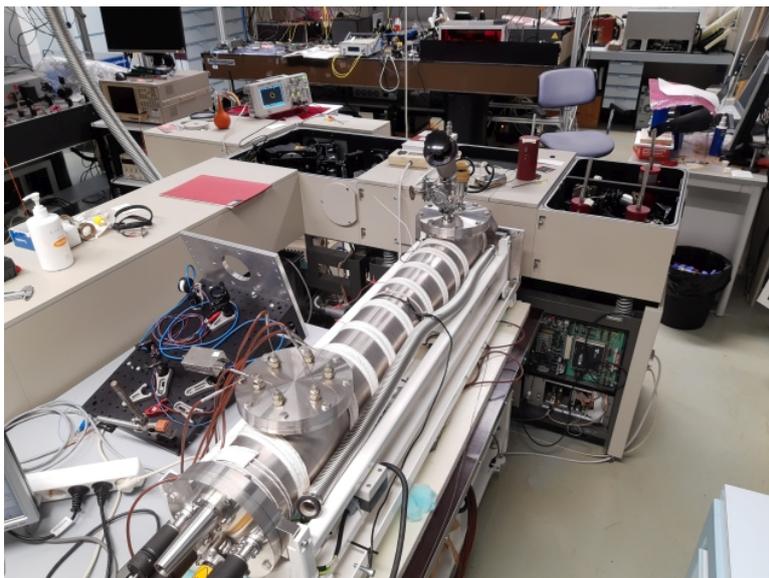


Figure 1. High resolution FTIR, Bruker IFS 120 HR, was used to measure the fundamental (in mid infrared spectral region) and the first overtone (near infrared) rotational-vibrational transition bands of H³⁶Cl.

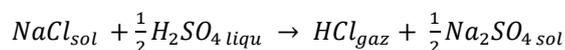
Table 1. FTIR settings used for the measurement of the fundamental transition band of H³⁶Cl.

Light source	Globar
Beam splitter	Ge-on-KBr
Detector	InSb
Aperture diameter	1 mm
Apodization function	Norton-Beer medium
Assumed HWHM of ILS function	0.0095 cm ⁻¹ (285 MHz)
Number of co-added interferograms	10
Type of interferograms	Double-sided
Interferogram processing method	Mertz
Zero-filling factor	2
Optical band-pass filtering	2614–3378 cm ⁻¹
Digital band-pass filtering	10–20 kHz (1975–3950 cm ⁻¹)
HeNe reference laser down-converted frequency	80 kHz

Table 2. FTIR settings used for the measurement of the first overtone transition band of H³⁶Cl.

Light source	Tungsten
Beam splitter	Si-on-CaF ₂
Detector	InSb
Aperture diameter	1 mm
Apodization function	Norton-Beer medium
HWHM of ILS function	0.0095 cm ⁻¹ (285 MHz)
Number of co-added interferograms	100
Type of interferograms	Double-sided
Interferogram processing method	Mertz
Zero-filling factor	2
Optical band-pass filtering	6667–5000 cm ⁻¹
Digital band-pass filtering	25–35 kHz (4937–6912 cm ⁻¹)
HeNe reference laser down-converted frequency	80 kHz

Samples for the experiments were generated from an aqueous NaCl-solution that had been enriched with ^{36}Cl (certified concentration of 0.1 mCi/ml). The solution was purchased from American Radiolabeled Chemicals, Inc. The solution was pipetted into a FTIR sample cell and dried so that solid NaCl remained (Figure 2). Gaseous HCl was generated from solid NaCl by a reaction with concentrated sulphuric acid in the sealed sample cell. The reaction equation is presented below:



Radioactive ^{36}Cl yield into gas phase was ~43% and the H^{36}Cl gas final concentration in the cell was 2750 ppm. This procedure to prepare gaseous ^{36}HCl sample was necessary since there are no commercial standard available in gaseous phase. In addition, this procedure has the advantage of producing only a small amount of water vapour, which can interfere with the measurement of HCl absorption lines.



Figure 2. Gaseous sample of H^{36}Cl was prepared by drying aqueous solution of Na^{36}Cl in the sample cuvette. In the figure above, dry air is flowed through the cuvette. After only solid NaCl was left in the cuvette, few drops of concentrated sulphuric acid was added to the cuvette. Then cuvette was sealed and tilted so that reaction between acid and NaCl started and produced gaseous HCl inside the cuvette.

3. Results

The 100% transmission baseline was determined manually from the HCl spectrum by first low-pass filtering the spectrum, excluding the HCl peaks from the data, and finally by using Savitzky–Golay filtering (Savitzky and Golay, 1964) and defining the result as the baseline. The spectrum was then divided by this baseline to obtain the HCl transmission spectrum. The result was further converted into absorption spectrum using the Napierian Beer–Lambert law. The resulting absorption spectrum is shown in Figure 3, where the measured fundamental rotational-vibrational transition bands is also compared with a simulation generated using information from the HITRAN-database (Gordon *et al.*, 2017)

The absorption lines were fitted in order to obtain the absorption line parameters and in particular the line centres and line intensities, which are the most relevant parameters to identify the most suitable line for detection via laser spectroscopy. Due to the relatively high measurement pressure (1 atm), pressure broadening dominates most of the transition linewidths. For this reason, it was chosen to model the absorption peaks as Lorentzian functions. All of the 21 rotational components (lines P(10)–R(10)) of the H^{36}Cl fundamental band were fitted separately such that a typical fitting window was $4\text{--}9\text{ cm}^{-1}$ around the H^{36}Cl peak in question. An example fit is shown in Figure 4 b) for line R(3). The fit model consists of three Lorentzian functions (one for each HCl isotopologue), a constant background offset, and a sine function to consider etalon effects. The obtained results from this procedure are compiled in Table 3, Table 4, Table 5 and Table 6 for the fundamental (in mid infrared spectral region) and the first overtone (near infrared) rotational-vibrational transition bands of HCl isotopes.

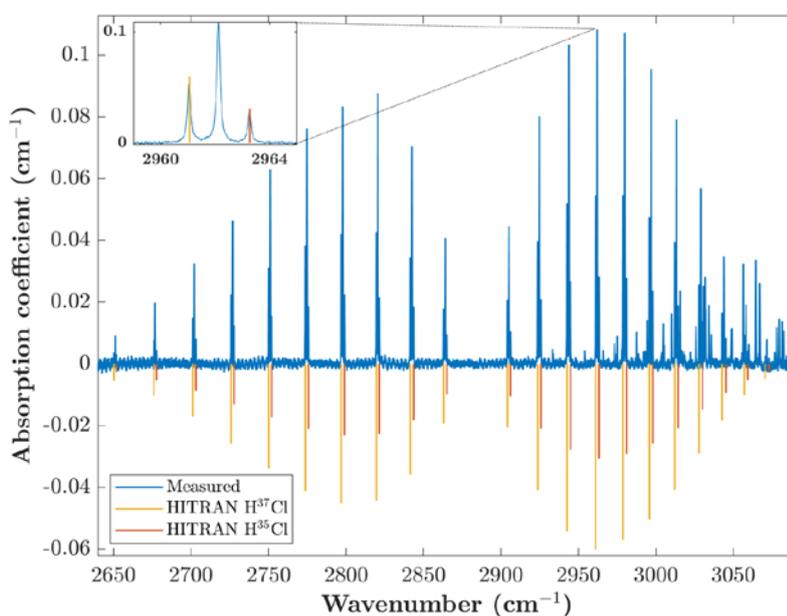


Figure 3. Measured absorption coefficient spectrum in the mid infrared spectral region. Peaks pointing down represents HITRAN simulation of fundamental rotational-vibrational transition bands of stable isotopes H^{37}Cl and H^{35}Cl . Zoom-in shows one transition for both stable isotopes and in the middle, transition for the radioactive isotope H^{36}Cl .

Table 3. Experimentally determined line parameters for the H^{36}Cl first overtone band. $\tilde{\nu}$ represents line centre wavenumber. $\sigma\tilde{\nu}$ represents the combined effect of the fit and calibration uncertainties (68% confidence level). Line centres are reported in 1 atm pressure.

Line	$\tilde{\nu}$ (cm^{-1})	$\sigma\tilde{\nu}$ (10^{-3} cm^{-1})
P(1)	5645.043(5)	7
R(0)	5685.525(5)	6
R(1)	5703.965(3)	5
R(2)	5721.168(2)	5
R(3)	5737.113(2)	4
R(4)	5751.802(2)	4
R(5)	5765.227(2)	4
R(6)	5777.370(3)	5
R(7)	5788.217(4)	5

Table 4. Experimentally determined line parameters for the H^{36}Cl fundamental band. Line centres are reported in 1 atm pressure.

Line	$\tilde{\nu}$ (cm^{-1})	$\sigma\tilde{\nu}$ (10^{-4} cm^{-1})
P(10)	2651.0675(13)	18
P(9)	2676.8101(6)	14
P(8)	2702.0639(4)	13
P(7)	2726.8168(3)	13
P(6)	2751.0527(2)	13
P(5)	2774.7574(2)	13
P(4)	2797.9207(2)	13
P(3)	2820.5297(2)	13
P(2)	2842.5712(3)	13
P(1)	2864.0247(4)	13
R(0)	2905.1493(4)	13
R(1)	2924.7790(2)	13
R(2)	2943.7809(2)	13
R(3)	2962.1397(2)	13
R(4)	2979.8392(2)	13
R(5)	2996.8709(2)	13
R(6)	3013.2251(2)	13
R(7)	3028.8887(3)	13
R(8)	3043.8510(4)	13
R(9)	3058.1013(6)	14
R(10)	3071.6279(13)	18

Table 5. Fundamental band molecular constants for H^{36}Cl . $\tilde{\nu}_{v=0}$ is the band center, \tilde{B} is the rotational constant, and \tilde{D} and \tilde{H} are the different order centrifugal distortion constants.

Parameter	Experimental (cm^{-1})	Predicted (cm^{-1})
$\tilde{\nu}_{1-0}$	2884.8936(3)	2884.8933
\tilde{B}_0	10.43210(4)	10.43213
\tilde{B}_1	10.12843(4)	10.12847
$\tilde{D}_0/10^{-4}$	5.275(3)	5.273
$\tilde{D}_1/10^{-4}$	5.207(3)	5.206
$\tilde{H}_0/10^{-8}$		1.66742

Table 6. First overtone band molecular constants for H^{36}Cl .

Parameter	Experimental (cm^{-1})	Predicted (cm^{-1})
$\tilde{\nu}_{2-0}$	5665.895(10)	5665.898
\tilde{B}_2	9.8274(8)	9.8272
$\tilde{D}_2/10^{-4}$	5.18(11)	5.15

Here, we briefly review estimated parameters from deliverable D5.1. In that document, a suitable H^{36}Cl transition line was estimated to be at 5737.138 cm^{-1} (at 1 atm pressure, see the top figure in Figure 4). In our experimental work, this line transition line was confirmed to lie at 5737.113 cm^{-1} (at 1 atm pressure) The combined effect of the fit and calibration uncertainties at 68% leads to a confidence level of $4 \cdot 10^{-3} \text{ cm}^{-1}$. This transition is then confirmed to lie in the laser emission range of the PROCEAS H^{36}Cl analyser designed in D5.1.

Unfortunately, the obtained experimental data for the first overtone transition (in near infrared region) was of too low quality to make meaningful estimation of the spectral line intensity for the H^{36}Cl transition at 5737.113 cm^{-1} . As an example, in Figure 4 is compared one of the strongest first overtone transitions (top figure) to the one of the strongest fundamental transitions (bottom figure). One can only conclude that there is no reason to suspect the estimated line intensity reported previously in D5.1. In that document, the line intensity was estimated to be $8.242 \cdot 10^{-21} \text{ cm}^{-1}$ when calculated as the average of H^{35}Cl and H^{37}Cl transition intensities but average should be calculated from raw spectral line intensities. This would yield estimation of raw spectral line intensity $1.647 \cdot 10^{-20} \text{ cm}^{-1}$, but the difference to the reported value in D5.1 is small so that the conclusions in D5.1 are still valid. As stated in D5.1, one should be able to achieve detection limit of ~ 1 ppb for H^{36}Cl in gaseous phase with CRDS.

Our experimental work yielded thorough data for the fundamental band of H^{36}Cl rotational–vibrational transition band in the mid infrared spectral region. In this fundamental band, spectral line intensities are typically ten times stronger than first overtone line intensities. In theory, this would result ten times lower detection limit. For the next iteration of the instrument reported in D5.1, it is advised to design the instrument so that it probes these transitions in the mid infrared spectral region. In this region, it should be also possible to find transitions, which do not suffer so much from spectral interference caused by water molecules. The latest development in instrumentation in this wavelength range can provide the required components (mainly lasers, detectors and high-reflectivity mirrors) to build a suitable CRDS system.



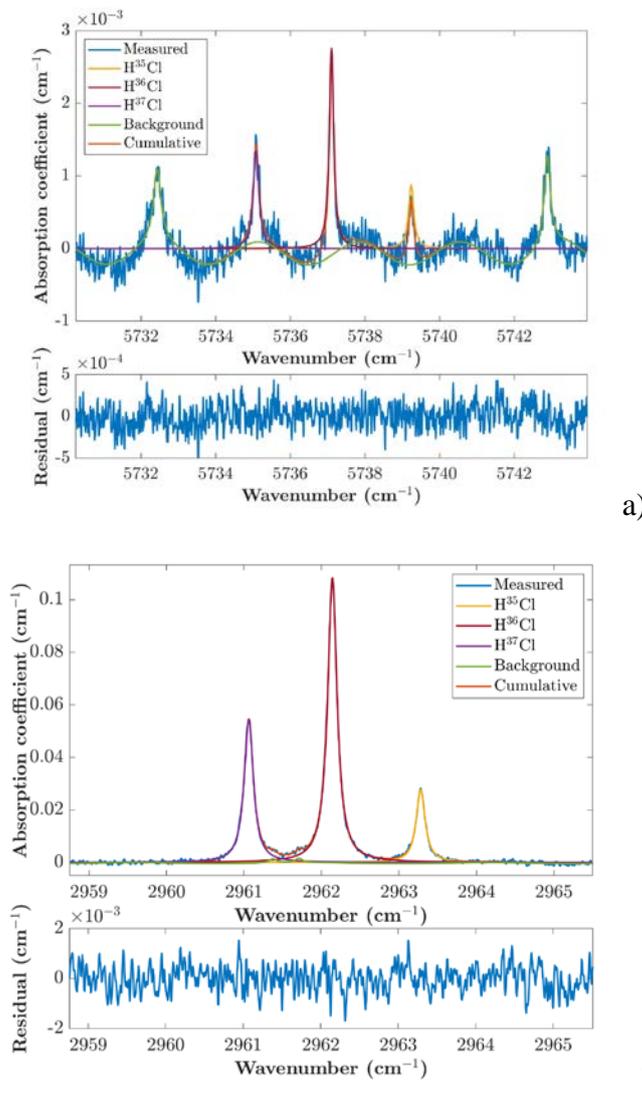


Figure 4. In top figure, first overtone transitions of HCl in the near infrared spectral region are shown with some background absorption caused by water molecules. In the bottom figure, fundamental transitions of HCl are shown in the mid infrared spectral region.

4. Conclusions and outlook

In nuclear decommissioning and in nuclear waste sites, H³⁶Cl is most likely encountered in very low concentrations. Laser spectroscopic methods can provide affordable and field deployable instruments to detect these trace amounts of H³⁶Cl. Cavity ring-down spectroscopy is one of the methods that provides highest sensitivities. To aid the development of these high sensitivity instruments, we experimentally determined the majority of fundamental and first overtone rotational-vibrational transitions of H³⁶Cl in gaseous phase. This was the crucial first step for the development. It is now expected that such a cavity ring-down spectroscopic instrument is able to achieve ~1 ppb, sensitivity for H³⁶Cl. If one needs even lower sensitivity, one can design the instrument to operate in mid infrared spectral region. However, this would increase the cost of the instrument and slightly add complexity of the system.

One major hurdle to consider is the design of a suitable sampling system. HCl is a very reactive gas which will be adsorbed on every surface. It is therefore preferred that measurements take place with flowing samples, which can be a challenge when small amounts of samples are available, e.g. in the case of nuclear waste outgassing. In addition, it is also crucial to remove water vapour from the sample to be analysed to minimise interference with the HCl absorption lines.

5. Bibliography

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