



Pressure control of tritiated hydrogen isotopologues in hermetically sealed vessels by non-evaporable getters for sub-Doppler-resolution spectroscopy

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ABSTRACT

Small molecules serve as valuable benchmarks for testing quantum chemical theories. Ultra-high-resolution spectroscopy currently offers the capability of measuring molecular hydrogen energy levels with a relative accuracy on the order of 10^{-10} . Expanding such investigations to encompass different isotopologues of molecular hydrogen has emerged as a promising avenue for examining mass-dependent contributions to the full description of molecular structure in the framework of relativistic quantum electrodynamics. However, the delicate nature of handling radioactive tritium in a high-resolution spectroscopy environment poses significant technological challenges, thereby limiting the extension of these studies to include T_2 , DT and HT isotopologues. In this work, we present the experimental setup of the very sensitive, Doppler-free technique of Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS), used to measure rovibrational transitions in the HT molecule. The NICE-OHMS measurements were performed in a closed cavity system without connection to an actively pumped vacuum system. For this reason, a new method for tritium storage and pressure regulation within 0.05–1 Pa based on a temperature-controlled mini-getter system is employed using less activity than the tritium exemption limit (1 GBq). Non-Evaporable Getters of the type SAES St171 were used for this purpose exploiting their property that hydrogen is released upon heating, while other gases remain being pumped. Prior to the NICE-OHMS experiment, the reversible sorption properties of the getter for hydrogen isotopes were investigated. We show measurements of the equilibrium (hydrogen) pressure for all three pure isotopes and for a H_2 :HT: T_2 mixture (with H:T = 1:1) as a function of temperature for a system of defined volume and amount of gas. For the read-out of the temperature, a method using the resistance of the getter in combination with a pyrometric calibration has been implemented. We discuss the experiences from practical use of the tritium getter and show results obtained with the NICE-OHMS setup leading to frequency calibration of near-infrared transitions in HT at an accuracy, surpassing previous studies by nearly three orders of magnitude.

1. Introduction

Molecular hydrogen is a benchmark system for precision tests of quantum chemical calculations. A comparison of high-precision spectroscopic measurements of transitions in these systems against their theoretical predictions can validate the theory of quantum electrodynamics (QED) in molecules. Recent high-precision measurements for benchmarking the dissociation and ionization energies of non-radioactive isotopologues, H_2 [1], HD [2], and D_2 [3] agree with theory at the 1 MHz level. The theoretical description includes a 4-particle variational approach to the non-relativistic Schrödinger equation, added with computation of relativistic and QED effects up to ma^6 [4–6].

For species as light as hydrogen a test of QED can be considered a test of the Standard Model of physics, since the effects of the weak and strong force are negligibly small. The precision tests in hydrogen can be interpreted to pose constraints on fifth forces [7] and higher dimensions [8], as well as to probe aspects of beyond the Standard Model physics [9].

By including tritium to the palette of targeted species, the number of molecular test species is doubled by adding T_2 , HT, and DT. The strong mass effects of the heavier isotopes may provide insight in the contributions of (non)-relativistic and various orders of QED terms to level energies and transition frequencies. However, the number of high-precision studies on these radioactive molecular hydrogen species is

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relatively small, which is due to limited access and radiation-safety issues. Outside of licensed laboratories, radioactive substances are restricted to an exemption limit by European law — in the case of the radioactive hydrogen isotope, tritium, this limit is the amount equivalent to an activity of $A = 1 \text{ GBq}$. This can be translated into a material content of $\rho V = 1159 \text{ Pa cm}^3$ (at 20°C) of tritium in its molecular form T_2 . For performing high-resolution spectroscopy on tritiated molecules, either the technological challenge of safe confinement and processing with this little amount of material must be overcome in a dedicated laser-based laboratory, or the spectroscopy including high-accurate and stable frequency standards must be moved inside a licensed tritium laboratory. Here the strategic choice was made for the former option.

This choice for small amounts of gases imposes challenges for laboratories in which high-resolution spectroscopic measurements are to be carried out. In many studies the technique of molecular beams is applied, requiring high-pressure sources as well as continuous pumping of connected vacuum chambers delivering large gas loads to an exhaust line. This is incompatible with the restriction to small gas samples. The nature of tritium as a high-energy β -emitter is also a limiting factor. In many experiments on molecules action spectroscopy, like multi-photon ionization, is employed for sensitive detection. For tritium-containing samples, intrinsically producing large amounts of energetic electrons, such methods are not viable in view of the large background signals swamping the ion detectors. Such constraints then leave possibilities to perform measurements on static gas samples, preferably combined with optical detection of the spectroscopic signal.

As an example, we performed Coherent Anti-Stokes Raman Spectroscopy (CARS) of the tritiated molecular hydrogen species HT, DT and T_2 ($\text{D} = {}^2\text{H}$, $\text{T} = {}^3\text{H}$) [10–13] by moving a sealed-off tritium sample in an optical cell from the Tritium Laboratory Karlsruhe (TLK) to LaserLaB Amsterdam. Fundamental vibrational transitions ($v = 1 \leftarrow 0$) have been determined to accuracies of 10 MHz. Compared to previous state-of-the-art spectroscopic accuracy [14,15] this entailed a factor of 100 improvement. Limiting factors of this technique were in the use of pulsed lasers for the generation of CARS signals at the prevailing pressures of up to 250 Pa in cells of volume 4 cm^3 , where the resolution was limited by Doppler broadening.

In parallel, developments in cavity-enhanced spectroscopy [16] have led to the direct absorption measurement of very weak ($v = 2 \leftarrow 0$) overtone rovibrational transitions in HD, in combination with accurate frequency-comb calibration of their center frequencies. Precision measurements in the Doppler-broadened regime [17–19] were superseded by intracavity saturation experiments at Doppler-free resolution [20, 21]. Although still some not-understood phenomena of intracavity non-linear optical spectroscopy persist [22–25], the frequencies for a variety of lines in the (2–0) band of HD have now been determined at an accuracy better than 100 kHz. In these studies it was found that the resonance frequencies undergo collisional shifts, prompting the need to perform measurements at low and well-controlled pressures.

The NICE-OHMS-technique, that was applied for the sensitive and ultra-high resolution measurements on the HD isotopologue at the Amsterdam LaserLaB [21,22,24], was adopted as a technique of choice to extend measurements to the radioactive molecular hydrogen isotopologue HT. For this purpose a dedicated cavity was constructed to perform laser spectroscopic measurements at variable density of the target species (HT), and with very low residual background pressure, outside of a licensed tritium laboratory using less than 1 GBq activity. A key component is the non-evaporable metal getter (NEG) (SAES St171) that allows provisioning of HT samples at different and well-controlled pressures in a closed setup through its ability to reversibly absorb hydrogen when heated.

The ability to trap and release hydrogen was tested prior to the spectroscopy campaign in a sorption study. The range of parameters (amount of gas, volume, and pressure range) is chosen to fulfill requirements of the targeted NICE-OHMS measurement campaign or those of comparable future experiments. The results for gases H_2 , D_2 , T_2 and

a $\text{H}_2\text{:HT:T}_2$ mixture (with $\text{H:T} = 1:1$) are presented and compared to discuss a potential isotope effect. As sorption properties for this getter are temperature dependent, an in situ temperature read-out is developed.

In this report, we present the experiences of the $\sim 300 \text{ h}$ operation time of the getter system for NICE-OHMS on HT including over 150 sample production cycles with tritium. The first spectroscopic results at sub-Doppler precision, presented in a separate publication [26], underline the success of this approach.

2. High-resolution spectroscopy on molecular tritium using NICE-OHMS

2.1. Concept of NICE-OHMS

Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) is a sensitive absorption-based spectroscopy technique that unites the methods of cavity enhancement and frequency modulation spectroscopy (FMS). The technique was invented by Ye and Hall [27], and some important development steps were attained by the group at Umeå university [28–30]. The tuneable laser at frequency f is phase-locked to the optical high-finesse cavity, leading to a lowering of its noise at short times. At longer time scales the drift of the cavity is piezo-electrically corrected for by the lock of the spectroscopy laser to a frequency comb laser. The high finesse of the cavity yields an enhancement of the interaction path length of the light beam through the sample. This leads to a high absorption sensitivity that allows spectroscopic measurement of very weak vibrational transitions in heteronuclear hydrogen isotopologues like HD, even for the (2–0) overtone band (dipole moment of $\sim 2 \times 10^{-5} \text{ D}$ [31]). By modulating the laser frequency f with a frequency equal to the free spectral range (FSR) of the cavity f_{FSR} two opposite-phase sidebands with frequencies $f \pm f_{\text{FSR}}$ are generated such that FMS can be performed within the cavity. This allows for a much more sensitive dispersion measurement with near shot-noise limited performance. Furthermore, the presence of high-intensity counter-propagating beams inside the cavity forms the condition to observe Lamb dips, enabling spectroscopy in the sub-Doppler regime [30]. NICE-OHMS combines high sensitivity and high accuracy, which renders it therefore an ideal method to investigate ro-vibrational transitions of molecular hydrogen isotopologues. For achieving high accuracy on the quantum level splittings in the molecule it is of importance to perform measurement at low and controlled pressures, without background gases. This is accomplished by the use of Non-Evaporable Getters (NEG) as is documented in the present study.

2.2. Requirements to NICE-OHMS with tritium

The tritium activity stored in the spectroscopy cell transferred from the TLK to LaserLaB Amsterdam is legally constrained to $A < 1 \text{ GBq}$.

Tritium exhibits significant radiochemical activity as a result of the production of molecular, ionic, and radical species resulting from its β decay. These highly reactive components can initiate secondary reactions when other species, such as hydrocarbons, are present [32,33]. In particular, it is crucial to avoid halogen-containing components as their radiation-induced decomposition can lead to the formation of chemically aggressive halogen hydrides/tritrides (e.g., TF , TCl , etc.) [34–36]. NICE-OHMS is a sensitive method and its performance deteriorates due to absorption by impurities in the sample or degradation of the highly reflective mirrors. To prevent such impurity generation in the sample and maintain the integrity of structural materials, especially highly reflective mirrors, it is necessary to construct a cavity that is free of plastics, rubber, oil, and similar organic materials.

Pressure affects the linewidth of the targeted spectral resonances, while the center frequency of the absorption features undergoes a pressure-induced shift [21,37]. These phenomena hold for the partial pressure of the hydrogen isotopologues under investigation as well

as for that of background gases. For spectroscopy at the sub-Doppler level, a quantitative attribution of pressure effects is mandatory [24]. Therefore, measurements at different sample pressures are necessary so that an extrapolation to $p = 0$ Pa can be performed. Pressure regulation is usually implemented by leaking gas from a container and removing it via conventional pumps. However, for operation with tritium in a sealed-off environment other solutions have to be found.

Here, a method has been developed allowing for spectroscopic measurements on HT samples in an optical resonator at different pressures, where the configuration combines the possibility of evacuation with the restriction of a small reservoir with the limited amount of tritium. For a proper quantification during spectroscopy, the composition of the gas sample must be stable during the measurement campaign.

The preferred method involves the use of Non-Evaporable Getters (NEG) and their capability to reversibly absorb hydrogen isotopologues. Upon activation through heating in a vacuum, NEGs dissociatively absorb non-noble gas molecules into their bulk. With the exception of hydrogen isotopes, all other atomic species remain permanently trapped. In the case of hydrogen, an equilibrium pressure is established above the getter surface, as a function of the quantity absorbed and the temperature of the getter.

The application of NEG in tritium technology is not entirely unprecedented. James et al. explored the utilization of NEG for tritium recovery from molecules, such as ammonia, that dissociate in the getter subsequent after their absorption [38]. For tritium extraction from breeding blankets in fusion reactors, helium is intended to be employed as a purge gas wherein tritium accumulates. Substantial quantities of NEG will thus be utilized to remove the tritium in a semi-continuous process, enabling its return to the fusion chamber [39]. Santucci et al. further evaluated this capability to eliminate tritium impurities as well from the helium coolant of breeding blankets in fusion reactors, where it permeates in trace amounts, but should be as free as possible from tritium [40].

In addition to their extensive application in fusion-related activities, NEG have been utilized for the precise dosing of small quantities of tritium and/or deuterium gas. Specifically, the Project8 experiment employed similar types of getters to introduce minute amounts of tritium into a measurement cell [41], while Das et al. [42] and Yamamoto et al. [43] used NEG to supply fusion-based neutron sources with D_2 and T_2 : DT : D_2 , respectively.

In this work a special NEG, a St171 getter type from SAES, which will be used in NICE-OHMS to set the partial pressure of the target molecule HT in the range 0.05 Pa to 1 Pa within the volume of the optical resonator.

2.3. Concept of sample production and measurement using NEG

Key component of the sample storage and release element is the NEG by SAES of St171 LHI/1,5–7 type welded onto a CF16 electrical feedthrough as displayed in Fig. 1. The NEG has a cylindrical shape ($\ell = 7$ mm, $d = 1.5$ mm) and contains 31.5 mg zirconium powder as active material which is sintered with graphite powder around a 0.2 mm thick molybdenum wire acting as a heater. After thermal activation at $T = 900$ °C, this NEG type can absorb non-noble gases from a vacuum system through a reactive surface into the bulk when applying high temperatures $T \geq 450$ °C.

Unlike its effect on other non-noble gases, St171 does not form chemical compounds with hydrogen even for very high hydrogen concentrations of 10–20 LTorr/g. Instead, the hydrogen diffuses into the bulk forming a solution following Sievert's law for this type of getter:

$$\log(P) = 3.6 + 2 \log(C) - \frac{5200}{T} \quad (1)$$

Eq. (1) describes the relation between the hydrogen concentration inside of the bulk (C in LTorr/g) of the getter and the hydrogen partial pressure outside of it (P in Torr) which is highly temperature-dependent (T in K). At room temperature, the partial pressure is very

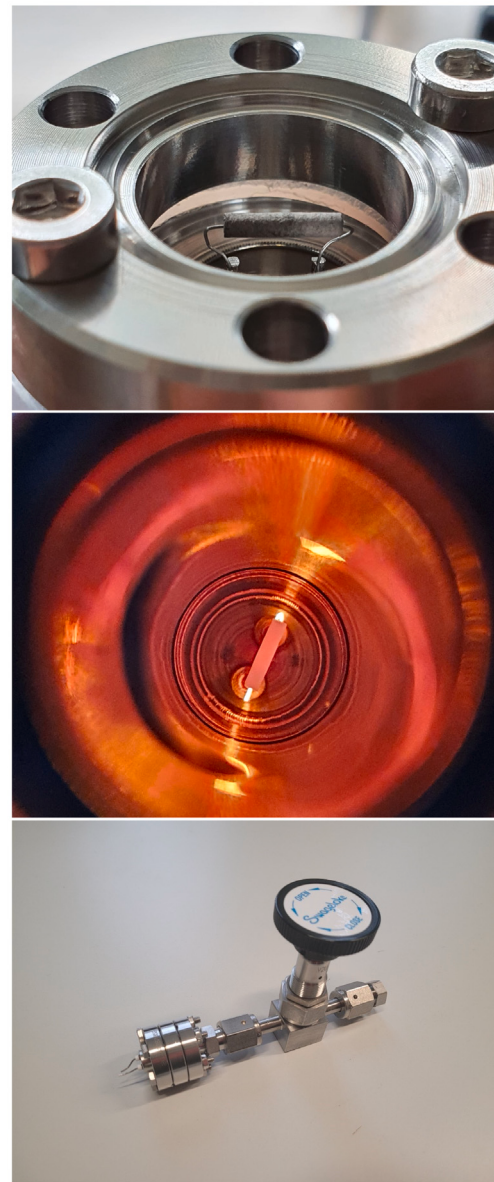


Fig. 1. Top: The St171 LHI/1,5–7 getter from SAES welded on an electrical CF16-feedthrough. Middle: View from location of the optical pyrometer during operation at 900 °C. Bottom: Getter installed in a small CF16-cell with a valve.

low, 1×10^{-10} Torr, which allows the use as a hydrogen pump. The material parameters in Eq. (1) are given by SAES.¹

The concept of sample generation and measurement can be divided in three main aspects: (a) tritium filling and shipment, (b) sample provision at target pressure, and (c) maintenance procedures that are implemented to guarantee stability and reproducibility of the samples:

(a) Filling and shipment of the tritium: The loading of the getter, encapsulated in a small CF16-cell with a valve (see Fig. 1(c) for connection to vacuum systems), is performed at the TLK tritium gas-mixture infrastructure TRIHYDE [44]. A defined amount of H_2 :HT: T_2 mixture (with H:T = 1:1) equivalent to 1 GBq activity is filled into the cell with the getter. The activated cold getter material absorbs the gas and traps it inside the bulk. After closing the valve and disconnecting

¹ SAES St171 and St172 - Sintered Porous Getters, <https://www.saesgetters.com/industrial/solution/non-evaporable-getters-neg/>.

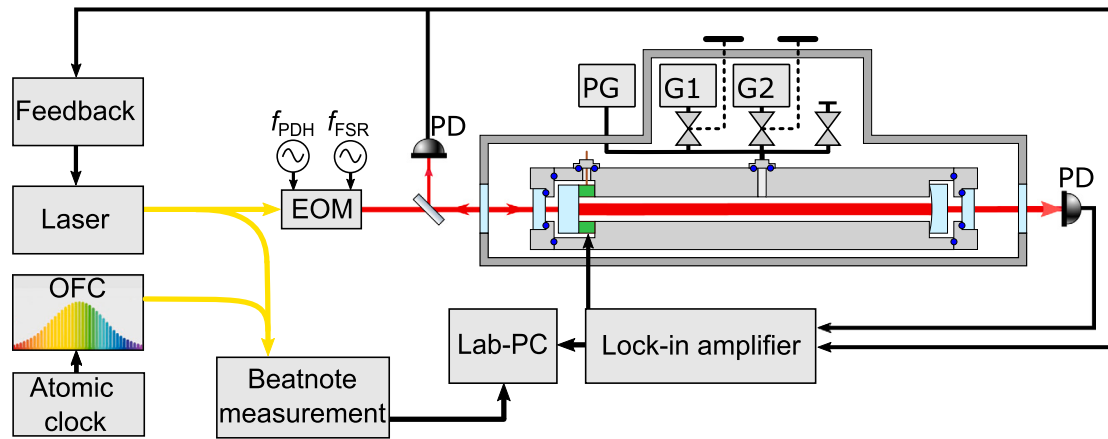


Fig. 2. Schematic layout of the NICE-OHMS experimental setup: On the left a diode laser is locked to a frequency comb laser (OFC) which itself is connected to a Cs atomic clock for determining the absolute frequency f . In the electro-optic modulator (EOM) sideband frequencies are generated for locking the cavity (via a Pound–Drever–Hall scheme — PDH) and for modulating the laser frequency with $f \pm f_{\text{FSR}}$ needed for the NICE-OHMS detection scheme. The 37 cm-long cavity is formed by two high-reflective mirrors setting up the high-finesse resonator. One of the mirrors is mounted on a piezo-electric crystal (green) for feedback and keeping the TM_{00} optical cavity mode to the input frequency during scanning. Vacuum of the cavity is maintained by slightly angled windows sealed by indium wires (indicated as blue dots). Connected to the cavity, there is a small getter (G1) containing the tritium-hydrogen mixture, a larger getter (G2) acting as vacuum pump, a process-monitoring pressure gauge (PG) and a connection to a pumping system which is sealed off before first tritium exposure. The entire cavity assembly is housed in a secondary, evacuated enclosure. Photodiodes (PD) are used to monitor the PDH-cavity locking signal, and for detecting the optical transmission signals to be demodulated and analyzed in a lock-in amplifier and further stored in a computer.

Table 1

Overview of the sources of systematic uncertainties resulting from each measurement device. As for the calibration several measurements have been combined some uncertainties may contribute several times to the results. Contributions can depend on the value (val.) as well as on the full scale (F.S.) of the device.

Device	Phys. quantity	Symbol	Description	1σ uncertainty
Pfeiffer CMR 365	Pressure	δ_p	Uncertainty	5×10^{-3} val.
			Resolution	3×10^{-5} F.S.
			Effect temp. on zero point	2×10^{-4} F.S.
			Effect temp. on range	3×10^{-4} val.
			Measurement gain error	1×10^{-4} F.S.
Pfeiffer TPG 362	Pressure	δ_p	Offset	1×10^{-4} F.S.
			Resolution A/D converter	1×10^{-5} F.S.
			Uncertainty	3×10^{-3} val. + 2°C
Optiris CTLaser 1ML	Temperature	δ_T	Transmission window	2°C
			Emissivity getter	2°C
			Uncertainty	0.01 val. + 3×10^{-3} A
Fluke 117	Current < 6 A	δ_I	Uncertainty	0.01 val. + 3×10^{-2} A
Fluke 117	Current > 6 A	δ_I	Uncertainty	5×10^{-3} val. + 2×10^{-3} V
Fluke 114	Voltage	δ_U	Uncertainty	

from the infrastructure, the outer surface of the cell is decontaminated and shipped to LaserLab Amsterdam where it is connected to the NICE-OHMS setup. A leak test and a cleaning cycle before shutting the setup guarantee the integrity of the system and allow the first tritium release.

(b) Sample preparation: To release the gas mixture and generate HT samples at specific pressure according to Sievert's law the getter material needs to be heated to a specific temperature. This is achieved by applying a DC current on the getter's wire heater. The temperature is read-out in-situ from the electrical resistance of the getter which has been previously calibrated against a pyrometer prior to the loading with tritium. The temperature range is from 500 to 900 °C. Sievert's law and material dependent parameters – describing the relation between the equilibrium pressure of the desorbed hydrogen above the getter surface and the temperature – is provided from SAES only for pure hydrogen. Therefore, a sorption study on this getter including all isotopes H_2 , D_2 and T_2 and a H_2 :HT: T_2 mixture (with H:T = 1:1) has been performed. A detailed description and results of this study are presented in the following section.

(c) Procedures maintaining sample integrity: (i) For optimal measuring conditions, high stability of the sample pressure and of the temperature of the cavity are required. The measurement can take several hours, and continuous heating of the getter is not advised as it would be detrimental to both stability criteria. A valve is used to decouple the getter from the cavity after setting the target conditions.

The getter can then be turned off and the thermal perturbation is reduced to a minimum. After measurement, opening the valve is sufficient for the sample gas to be reabsorbed by the tritium getter. Any tritium-hydrogen mixture that touches the getter material when cold will be absorbed. An accurate pressure read-out connected to the sample volume serves as the process monitor. (ii) Outgassing of hydrogen and residual water from the inner walls of a vacuum system can be a challenge, especially when the tritium vacuum system is decoupled from any exterior vacuum system due to radiation protection measures. Therefore, a getter of the same type as the tritium getter but with ten times more getter material is used as a vacuum pump to remove other species from the cell volume. This getter is separated with a valve from the sample volume to not interfere with sample production and is only used after measurement breaks of several hours. The pressure sensor connected to the sample volume serves as a process monitor. It should be noted that this vacuum getter is implemented to not burden the capacity of the tritium getter with outgassing residual gases. A change in the capacity of latter can alter its performance and, therefore, hamper the reproducibility of the sample production.

(iii) Despite these procedures, the production of (tritiated) water during measurements, possibly enhanced by the radiochemistry of tritium, cannot be excluded. To avoid any impact on measurement performance by absorption from (tritiated) water species, a cryo-trap cooled by LN_2 is implemented to freeze out any produced water or other species during measurements.

All procedures on preparation of samples of HT gas, filling getters, transport to LaserLab Amsterdam, evacuating the entire setup, were tested and spectroscopic measurements on HD spectral lines in its (2–0) band were performed in the same cell [45].

2.4. Experimental setup

The experimental setup for performing NICE-OHMS on HT gas in a radiation safe environment is depicted in Fig. 2. It consists of a fully custom-built cavity made with indium-sealed windows at each end. The cavity is machined out of solid aluminium so that the surfaces in contact with the hydrogen/tritium gas are less prone to wall-adsorption of the hydrogen molecules, compared to some glass materials (ULE) or stainless steel. The 37 cm long cavity is hemispherical with a curved mirror at a radius of curvature of 2 m. A triple-stack piezo-actuator at one of the mirrors allows for small-scale adaptation of the cavity length. A stainless steel tubing connection from the cavity grants access to a Pfeiffer 365CMR pressure gauge, a (larger volume) non-evaporable getter SAES St171 HI/7,5–7 acts as a vacuum pump and a (smaller volume) non-evaporable getter SAES St171 LHI/1,5–7 loaded with a $H_2:HT:T_2$ mixture (with H:T ratio = 1:1) equivalent to activity 1 GBq for the provision and removal of the HT sample from/to the volume of the laser-gas interaction. A connection to a pumping system was used prior to the first exposure to tritium to evacuate the system. Furthermore, an LN_2 -cooled cryotrap is included to capture any potentially generated (tritiated) water or other species. This part of the system exposed to tritium has a volume of $\sim 140\text{ cm}^3$ and has been tested for leaks to the detection limit of $1 \times 10^{-9}\text{ Pa L s}^{-1}$.

To isolate the cavity from acoustic and thermal disturbances, it is surrounded by a secondary enclosure evacuated below $1 \times 10^{-2}\text{ Pa}$. The valves between the attachments of the cavity assembly can be operated from outside of the secondary enclosure through rotational feedthroughs.

The laser beam, optics, photodetectors, electro-optic modulator (EOM), and further instrumentation are installed into another thermally isolated enclosure, flushed with dry nitrogen. Within this enclosure, NICE-OHMS relevant procedures as the locking of the laser to the cavity and generation and locking of the frequency-sidebands are implemented. Positioned behind the cavity, a fast-readout photodiode (New Focus 1611FS-AC) housed in a thermally isolated box records the signal. In a high-speed lock-in amplifier (Zurich Instruments HF2LI) both the high frequency phase modulation of the EOM and the low frequency dither on the piezo in the cavity are simultaneously demodulated. For the treatment of NICE-OHMS detection and demodulation schemes we refer to Refs. [21,22,24].

3. Sorption study with NEG tritium getters

For the NICE-OHMS experiment on HT, reversible tritium storage using the NEG St171 from SAES is a crucial asset, as it offers repetitive measurements with tritium at different pressures, although it is restricted to small activity. The performance of this component is depends upon the sorption characteristics of hydrogen isotopologues. The isotopic dependence on getter rates and equilibrium pressures has been previously examined for various getter materials (see [46, 47]). Although studies involving tritium are available (e.g. [43,48]), the detailed analysis of the behavior of this radioactive gas remains limited. Consistent findings indicate isotopic effects, notably manifesting as increased equilibrium gas pressure with larger atomic masses. Moreover, the significance of these isotopic effects varies markedly across different materials, emphasizing the necessity of conducting absorption/desorption studies on the selected getter material.

To determine these properties, a study on the SAES St171 getter using H_2 , D_2 , T_2 and a mixture of H_2 , HT, and T_2 (with H:T = 1:1) has been performed in the Tritium Laboratory Karlsruhe (TLK) prior to implementation into the NICE-OHMS experiment. This study is presented in the following.

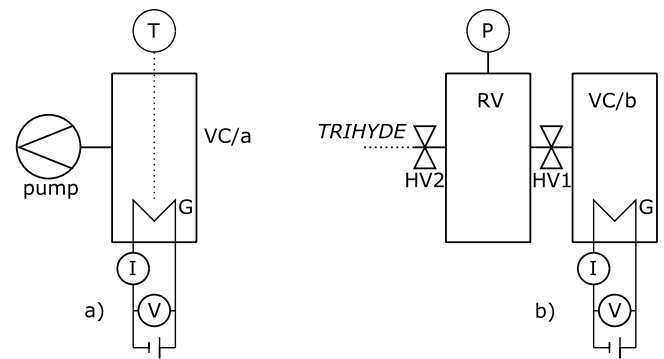


Fig. 3. (a) **Calibration system:** The SAES St171 LHI/1,5–7 getter (G) powered with current (I) and voltage (V) readout. A pyrometer Optris CTLaser 1ML (T) measures the temperature through a glass window. The vacuum cell (VC/a) is evacuated through a pumping system; (b) **Tritium system:** Consisting of vacuum cell of the getter (VC/b), reference volume (RV), a Pfeiffer CMR 365 pressure sensor (P) and valves (HV1&2) to separate vessels and the reference volume from the Tritium Laboratory Karlsruhe infrastructure TRIHYDE [44] providing tritium-gas mixtures and a pumping system.

3.1. Setup of the tritium sorption study

In the calibration procedure, we use one *calibration system* for the measurement of the current-temperature dependence, $I(T)$, and another, the *tritium system*, for the resistance-current, $R(I)$, dependence as part of the calibration process and for the actual sorption measurements including tritium. A schematic layout of both setups is presented in Fig. 3. The contributions of systematic effects by all measurement devices are listed in Table 1.

3.1.1. Calibration system

The *Calibration system*, displayed schematically in Fig. 3(a), consists of the welded getter mounted inside a vacuum cell (VC/a) and is faced by an optical pyrometer Optris CTLaser 1ML for measuring its temperature through a glass window. A connection to a pumping system is used to create and maintain vacuum conditions. The inner volume of the *Calibration system* is 30 mL.

3.1.2. Tritium system

The *Tritium setup*, displayed schematically in Fig. 3(b), reuses the same getter-feedthrough assembly as for the calibration to preserve the thermoelectrical properties. The vacuum cell (VC/b) is identical to the *Calibration system*, but with a blind flange replacing the pyrometer window. Using mostly the same parts as for the calibration, from the perspective of the getter the direct environment is identical within a 99.5 % of solid angle. Note that the geometry of the surrounding vessels affects the power balance of thermal radiation by a different fraction of losses and reflections. A reference volume (RV) combined with a Pfeiffer CMR 365 pressure sensor is connected by valves on either of the two sides to the getter cell (VC/b) and the tritium gas-mixture infrastructure TRIHYDE [44], respectively. The inner volume of the *Tritium setup* is 61.8(4) mL.

3.2. Procedure of getter temperature measurement and control

Hydrogen sorption by the St171 getter is temperature-dependent, cf. Eq. (1), thus reliable in-situ temperature measurement is mandatory. This can be performed using a pyrometric measurement approach. For the final getter assembly, incorporating such a sensor is very challenging due to experimental restrictions in (a) the tritium glove systems and (b) the NICE-OHMS setup.

The method of choice is to read the temperature from the electrical resistance of the getter heater itself, previously calibrated against the pyrometric standard. Note that the temperature of the getter material

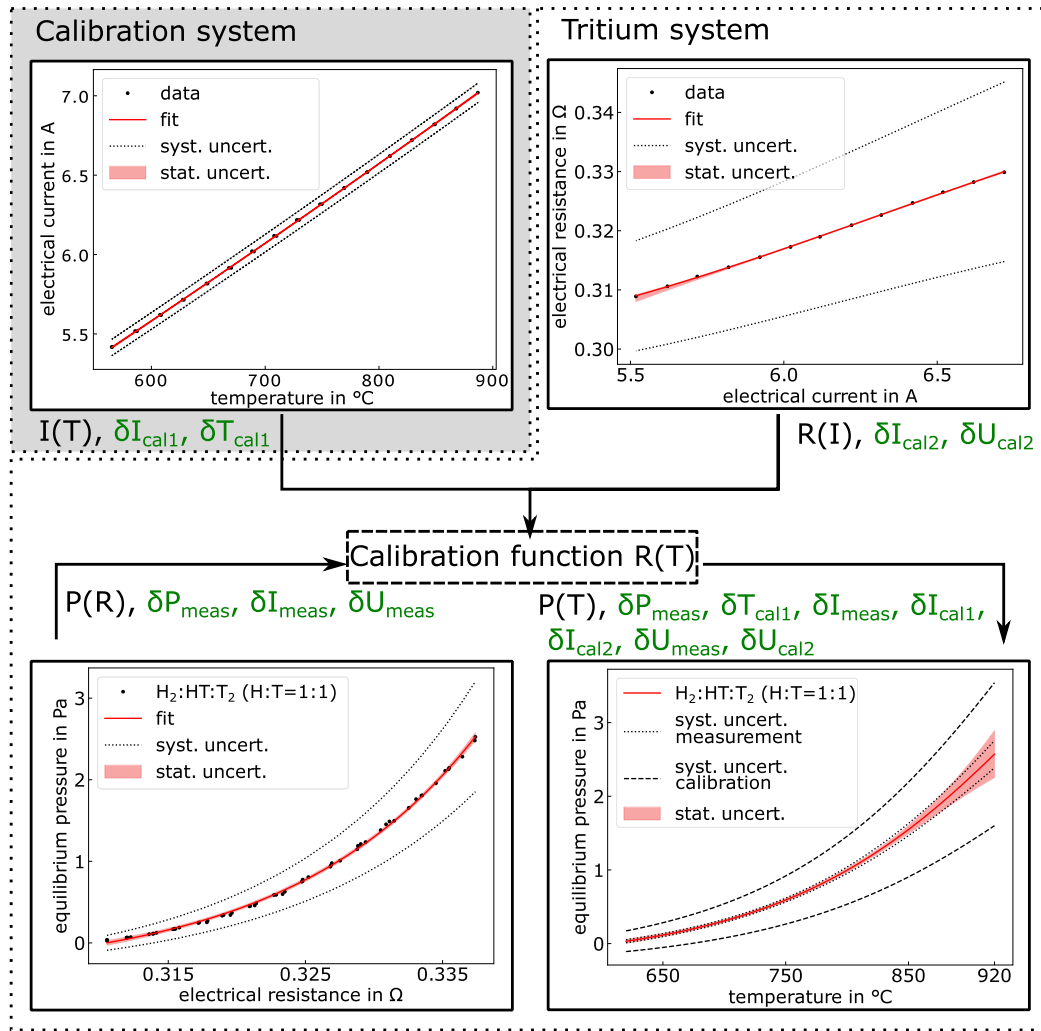


Fig. 4. The calibration and measurement procedure for the SAES getter hydrogen mixtures sorption study. Top left: Optical pyrometry together with a measurement of the operation current of the getter in a dedicated calibration system provide the relation $I(T)$. Top right: At the final location of the getter in the tritium system, the relation of resistance to heating current curve $R(I)$ are calibrated. Bottom left: In addition, in this system the pressure is measured with a pressure gauge as a function of the resistance $P(R)$. These functional dependencies are put together in order to obtain a relation of pressure and temperature in the actual sorption measurement, $P(T)$. The contributions to the systematic uncertainties have been indicated for each step in green with the symbol of the physical quantity. Values can be found in Table 1.

is not homogeneous throughout its surface. Differences of up to 20 K have been observed, which are taken into account when discussing the accuracy of temperature measurements or temperature-dependent effects.

The measurements are performed according to the concept depicted above in Fig. 4 with (i) measurements for the calibration of the temperature measurement and (ii) the sorption measurements for hydrogen mixtures.

3.2.1. Calibration of temperature measurement

The getter-feedthrough assembling is calibrated in a two-step process. First, the surface temperature (T) is measured in the Calibration system with an optical pyrometer as a function of the heating different currents (I) in steps of $\Delta I = 0.1$ A between 5.4 A and 7.0 A at high vacuum conditions ($< 4 \times 10^{-2}$ Pa). The upper limit for the temperature is $T_{\max} = 900$ °C which is recommended from the manufacturer SAES. In a second step, the getter-feedthrough assembly is installed inside the Tritium system at the tritium gas-mixture infrastructure TRIHYDE [44] of TLK. Under high vacuum conditions the electrical resistance (R) is measured for the same operation parameter as used in the calibration setup. Using the current-temperature relation $I(T)$ from the first (calibration) step and resistance-current relation $R(I)$ from the second step,

we obtain a functional relation of $R(T)$ during a measurement of the sorption at different operation powers.

3.2.2. Sorption measurements of hydrogen mixtures

Initially, the getter material is activated by operation for 10 min in a high vacuum at 900 °C. The necessary current to achieve that temperature is taken from the calibration process, here 7.0 A. For the comparability of sorption measurements of the different hydrogen mixtures, the amount of the investigated gas mixture has to be well defined. For that purpose, a reference volume (RV) with a capacitance pressure sensor (P), connected with a valve (HV1) to the cell (VC/b) with the getter (G), is filled with a defined amount of gas. The subsequent loading to the getter is then performed by opening valve HV1.

After opening the valve (HV1) to the getter cell the defined amount of hydrogen is absorbed by the getter, recorded by the drop in pressure below the lower range of the pressure sensor of $< 4 \times 10^{-2}$ Pa (except for tritium loadings where ^3He is remaining). During the measurements, the pressure of the desorbed gas, the electric current (I), and the voltage (V) applied to the heater of the getter are recorded for operating currents between 5.4 A and 7.0 A in steps of 0.1 A. For each current setpoint, a certain amount of time, typically about 5–10 min, has been spent to allow the stabilization of the system to be visible as the plateau of the pressure value.

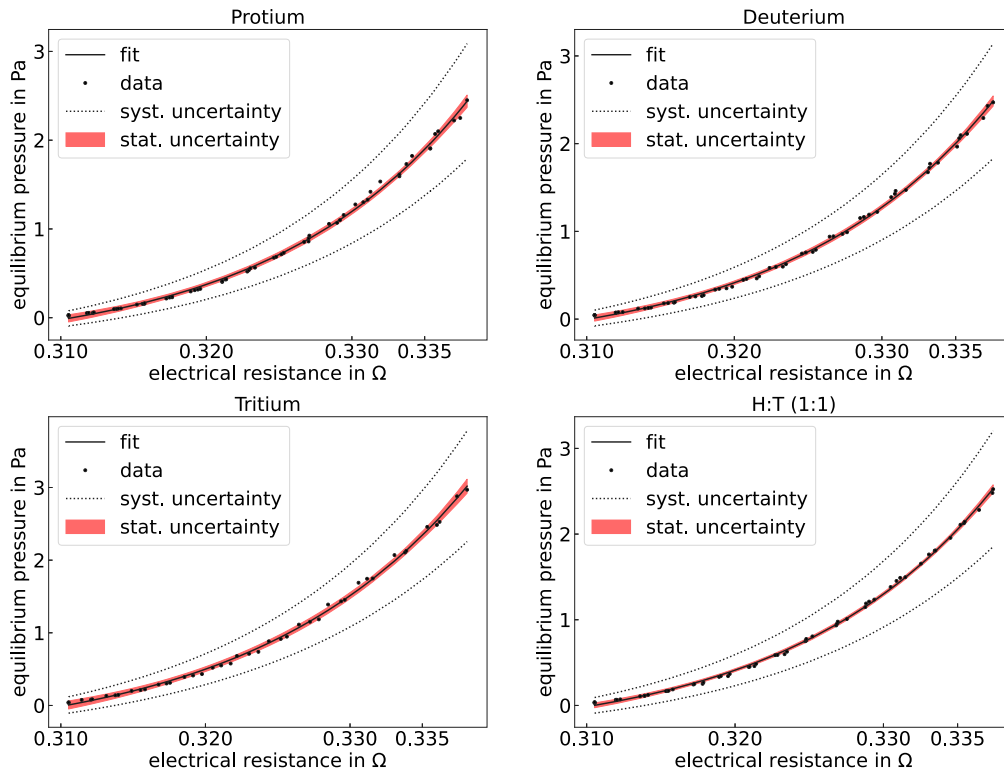


Fig. 5. Equilibrium pressures of the desorbed gas from a SAES St171 LHI/1,5–7 getter for almost equal H_2 , D_2 , T_2 and $H_2:HT:T_2$ mixture (with $H:T = 1:1$) loadings, and for operations between 5.4 and 7.0 A.

The unloading of the getter is performed by operation at 900 °C while evacuating for 30 min. Note that the duration of the unloading process depends on the loaded amount, pumping speed of the system, and the temperature of the getter. For the D_2 and H_2 measurements, the amount of 2.20(2) PaL is loaded at room temperature. For reproducibility proof, the H_2 measurement is repeated with equal amounts of gas.

The tritium gas available for the experiments contained about 2% of the tritium decay product 3He , which is not absorbed by the getter. For that reason, the loading of T_2 and of a $H_2:HT:T_2$ mixture (with $H:T$ ratio = 1:1) is performed with an additional step replacing the quantity of 3He left over after the first loading by the same amount of $\frac{1}{2}T_2$. The loaded gas amounts in this work are 2.22(2) PaL for T_2 and 2.21(2) PaL for $H_2:HT:T_2$. The amount of gas corresponds for a mixture of $H_2:HT:T_2$ (with $H:T = 1:1$) to a total activity of 1 GBq the maximum target condition for the NICE-OHMS experiment.

3.3. Results of the tritium sorption study

3.3.1. Calibration

The calibration is performed as described in the concept section and the procedure is sketched in Fig. 4. In the range of 5.4 to 7.0 A 34 temperature/current data points are recorded with the *Calibration System* to obtain the operating current-temperature function $I(T)$ by a second order polynomial fit. With the *Tritium system*, 25 data sets of applied voltage and current are measured from 5.4 to 7.0 A. The function $R(I)$ resulting from a third order polynomial fit of the voltage-current measurement and the function $I(T)$ are then combined to the calibration function $R(T)$. The systematic uncertainties resulting from the pyrometer, ampere meter, and voltage meter are taken into account, as well as the statistical uncertainties. In Fig. 4 the contributions are indicated in green with the symbol of the associated physical quantity. In Table 1 the individual contributions from each measurement device are shown. When propagating the calibration from the pyrometer to the resistance/temperature dependence of the getter,

these uncertainties lead to a rather high systematic uncertainty in the absolute temperature ($\Delta_{\text{sys}}T_{\text{calibration}} \approx 50$ K). This will affect the sorption curves of all species. The calibration fit parameters can be found in the Supplemental Material.

3.3.2. Sorption measurements

In Fig. 5, for four different gas samples, the recorded pressure is plotted as a function of the electrical resistance of the getter obtained from the voltage and current measurement. Note that the change of the electrical resistance is assumed to depend on the temperature of the getter. The four gas samples cover a pressure range from 3 Pa down to the lower range of the pressure sensor of 4×10^{-2} Pa. For H_2 , both measurements show no significant differences, thus demonstrating the reproducibility of the method. For each of the four samples, an exponential fit has been performed, showing a slightly different offset for each cycle in the electrical resistance. This offset is independent of the pressure in the cell and was found to increase during the measurement campaign. The data and the exponential fits are corrected by these systematic offsets using the mean value of the resistance of all measurements in operation at lowest pressure. Due to small differences in the offset of the resistance for each cycle, there is, in addition to the systematic uncertainty of the calibration, a second smaller systematic uncertainty ($\Delta_{\text{sys}}T_{\text{measurement}} \leq 7$ K) that affects the curves individually.

The temperature reading of the getter via the resistance of the getter has a rather high absolute uncertainty of $\Delta T_{\text{abs}} = 50$ K and a relative uncertainty of $\Delta T_{\text{rel}} = 7$ K. Considering a gradient of $\Delta T_{\text{spatial}} = 20$ K over the getter material, these high uncertainties might be acceptable and the method suitable for this application.

Fig. 6 shows a comparison of the pressure of the desorbed gases as a function of the getter temperature for the four samples, for which the parameters can be found in Table 2. Note that the parameters are presented with covariance matrix elements. The uncertainties stated to these parameters were found with Monte-Carlo to be in accordance with the statistical uncertainties.

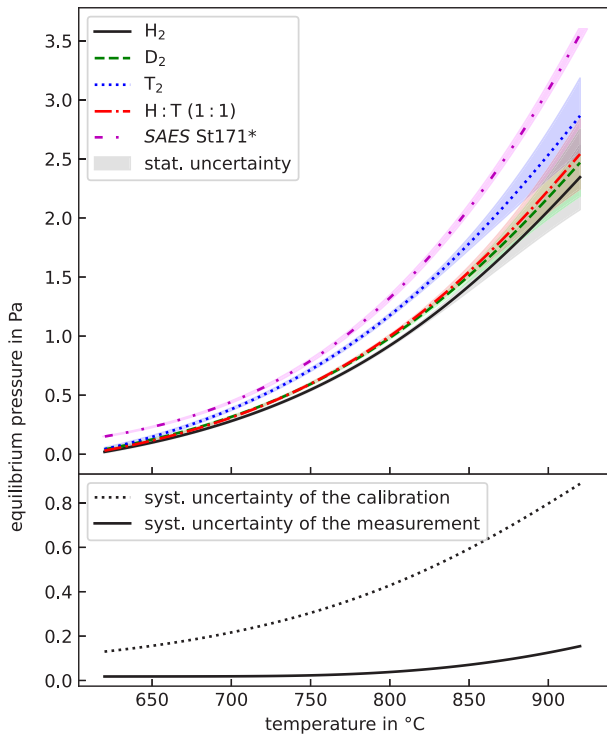


Fig. 6. Comparison of results of the sorption measurements for H_2 , D_2 , T_2 and the H_2 :HT: T_2 mixture (with $H:T = 1:1$) shown for the selected temperature operation range. The temperature was obtained from the measured electrical resistance translated using the temperature calibration method described. As the systematic uncertainty of the calibration affects all curves equally, while the systematic uncertainty of the measurements may be different for different measurements, the sources of systematic uncertainty have to be considered separately. Differences in the sorption for the different gas species can thereby be extracted. The expected pressures taking loaded amount, volume and getter properties from SAES are plotted for comparison.

Table 2

Obtained parameters for the desorbed hydrogen samples H_2 , D_2 , T_2 and HT with (almost) equal loadings in the sorption experiment. The fit function for the pressure is given with: $P = A \times \exp(B \times (T - 770)) + C$ in units of Pa and for temperatures (T) in °C. The measured electrical resistance has been obtained from the desorption measurement and is converted to a temperature using the calibration process described in the text. Note that these relations are only valid for the analyzed range. Uncertainties were derived using a Monte-Carlo approach. Covariance matrix elements Cov_{ij} are provided as well.

Gas species	H_2		D_2		T_2		HT	
Parameter	Value	2σ	Value	2σ	Value	2σ	Value	2σ
$A \times 1$	1.2	(0.4)	1.2	(0.4)	1.6	(0.7)	1.3	(0.3)
$B \times 10^3$	6	(1)	6	(1)	5	(2)	6	(1)
$C \times 10^1$	-4	(4)	-5	(4)	-7	(6)	-5	(3)
$Cov_{AB} \times 10^4$	-2		-2		-4		-1	
$Cov_{AC} \times 10^2$	-4		-4		-1		-3	
$Cov_{BC} \times 10^4$	2		2		3		1	

In addition, a calculated curve using loaded amount, volume of the system and getter properties from the manufacturer is included showing that the measured desorption is below expectations but in accordance for a systematic underestimation of the getter temperature by ΔT_{abs} .

Taking into account the statistical and individual systematic uncertainties $\Delta_{sys} T_{measurement}$, there are no significant differences in the desorption of the various hydrogen species at a temperature greater than 850 °C. For T_2 however, an overall higher pressure can be observed for temperatures below 850 °C. The curves for H_2 and D_2 in the measurement do agree on the level of the stated uncertainties. For the H_2 :HT: T_2 mixture, the curve lies between those of H_2 and T_2 , which implies that there are hints for different sorption properties for the isotopes.

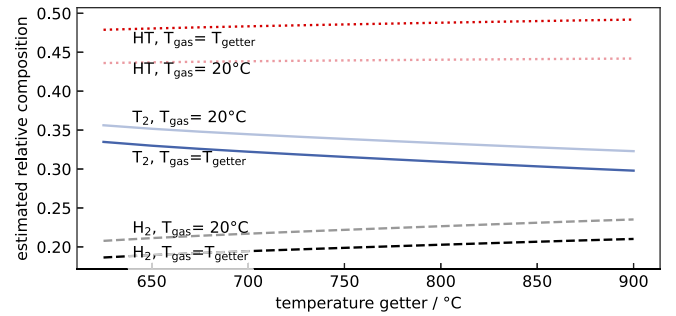


Fig. 7. The estimated composition of the desorbed gas from a St171 getter loaded with a H_2 :HT: T_2 mixture (with $H:T = 1:1$) based on the desorption results for the pure H_2 and T_2 gases. The equilibrium composition is calculated for the temperature of the getter and at 20 °C using the temperature dependent equilibrium constants from [49].

However, measured differences in desorption can affect the composition of the desorbed gas for isotope mixtures like the one here for the mixture H_2 :HT: T_2 . Based on pure T_2 and H_2 measurements, an estimation of the composition of the desorbed gas can be made using the following assumptions:

- Even at 900 °C more than 90% of the gas is solved in the getter material. Although the pressure outside of the material shows to be different for tritium and protium at the same temperature, the difference of concentration of hydrogen inside of the getter at each temperature can be neglected and is assumed to be same for H and T (difference of concentration < 1.5%)
- The different isotopes have very limited influence on each other inside of the bulk. This assumption may be justified in the given cases as the ratio of gas atoms to getter atoms is less than 6 ppm.

The recorded desorption pressures of H_2 and T_2 together with the temperature-dependent equilibrium constants for H_2 :HT: T_2 mixtures [49], the gas composition for a sample of a H_2 :HT: T_2 mixture (with $H:T = 1:1$) as a function of temperature can be estimated, as shown in Fig. 7. During desorption the gas temperature is significantly higher than after isolating it at room temperature which is the measurement condition in NICE-OHMS. The impact on the equilibrium constant leads to a shift in the composition as indicated in the figure. Throughout the operation range, the composition remains stable (change of concentration from peak to peak for HT < 0.7%).

4. Results of the NICE-OHMS experiment

4.1. Operation with tritium

The time between the loading of the getter with tritium at TLK and first NICE-OHMS experiments at LaserLab Amsterdam was 176 days including the decontamination, shipment, installation and procedural steps and associated delays. The decay of tritium into ^3He has an impact on the experiment as was noticed after opening the tritium getter to the NICE-OHMS system. An increase of the pressure by 0.085 Pa was observed, which was attributed to ^3He . As a noble gas, it cannot be pumped by the getter, and remains present as constant pressure offset inside the optical cavity. Using tritium's half life of ~ 4500 days [50] and the available volume of $\sim 140 \text{ cm}^3$ this released amount corresponds to about $\sim 20\%$ of the total ^3He generated from β -decay over the entire time span since the loading with tritium. It is well known, that ^3He can be trapped in metal after β -decay of tritium solved in the bulk (see e.g. [51]). The porous morphology of the getter implies a large surface that is favorable for its pumping speed but with solved tritium also leads to a comparably high helium release.

Long-term operation of the getters appeared to lead to instability of the cavity due to a minute thermal expansion. For that reason, an

alternative procedure for sample preparation has been employed. The tritium getter operates at a current corresponding to 850 °C with closed valve, and the pressure in the optical measurement cavity is set by controlled opening of the valve. The in situ temperature measurement has therefore only been included for monitoring the operation of the getter.

To return the tritium back to the getter, the valve to the getter-cell needs to be opened without heating the getter. Usually, after measuring a sample for several hours, it was necessary to reactivate the getter material by operating it at 850 °C with a closed valve for 2 min to restore pump performance.

The cryotrap was tested once for accumulated residual gases. Achieving temperatures down to 78 K no pressure reduction is observed. The residual gas is absorbed down to the ^3He pressure level by the cold vacuum getter and is therefore identified as mainly hydrogen. Thus, opening the valve to the vacuum getter without heating, as a cleaning procedure before the measurements, is often sufficient. Only after several cycles is a degradation of the pumping speed of the getter noticeable, a sign that the surface of the getter is blocked by nonhydrogen residuals. Then, an operation at a current corresponding to 850 °C is performed for less than 15 min.

During ~ 300 h of measurement and about 120 of sample provisions, no degradation of the getter/sample production performance is observed.

4.2. Spectroscopy performance of the system

Before actual HT measurements can be performed, adjustment and calibration of different parameters essential for the NICE-OHMS operation have to be prepared. Settings of the optical modulators, locking of the laser and its sidebands to the cavity and frequency comb, as well as phase settings of the lock-in amplifier, are typically tuned on a water line close to the frequency of the HT target line. For this procedure, the little amount of water vapor remaining after the cleaning cycles is sufficient. The water content decreased with repeated operations throughout the measurement campaign. An example of a single scan of the (J , K_A , $K_C = 6_{4,3} \rightarrow 5_{1,4}$) transition in the (000) $\rightarrow$ (200) band of H_2O is given in Fig. 8 showing the Doppler-free Lamb dip feature recognizable in its Lorentzian profile.

The optical cavity is built from two mirrors custom-produced by Layertec with a reflectivity of $R = 99.996\%$ for the wavelength of the laser (TOPTICA DL Pro) of $1430 \text{ nm} < \lambda < 1520 \text{ nm}$. The finesse of the cavity amounts to $F = 80000$ and is approximately the same in the wavelength range 1460–1510 nm in which the spectroscopic experiments are performed. This leads to an average circulating intracavity power of $P = 400 \text{ W}$, although for some measurements the power level is set lower. Over the course of the measurement campaign no tritium-induced degradation of the finesse, and hence the mirror coatings, was observed.

In total, three lines in the $\nu = 0 \rightarrow 2$ overtone band of HT are measured in the wavelength range 1460–1510 nm. Results of spectral recordings of the R(0), R(1) and P(1) lines are displayed in Fig. 8. Observed signal levels are proportional to the sample pressure and are reproducible throughout the campaign. While the spectroscopic analysis and the context of a comparison to results of QED calculations is presented in a previous report [26], some features are discussed here. Similarly as in the study of the HD (2–0) overtone transitions, again dispersive lineshapes are observed for the R(0) and R(1) transitions. This behavior has been observed in HD before [22,23,25,45,52] and is considered an unexplained conundrum. However, there occurs a marked difference between the spectra of HT and HD in that the HT isotopologue exhibits a single isolated hyperfine component in the R(0) and R(1) lines, allowing to determine the rovibrational transition frequency to an accuracy of 20 kHz. As a result vibrational level splittings can now be determined at the kHz level, where previous state-of-the-art only reached MHz accuracy [12,13].

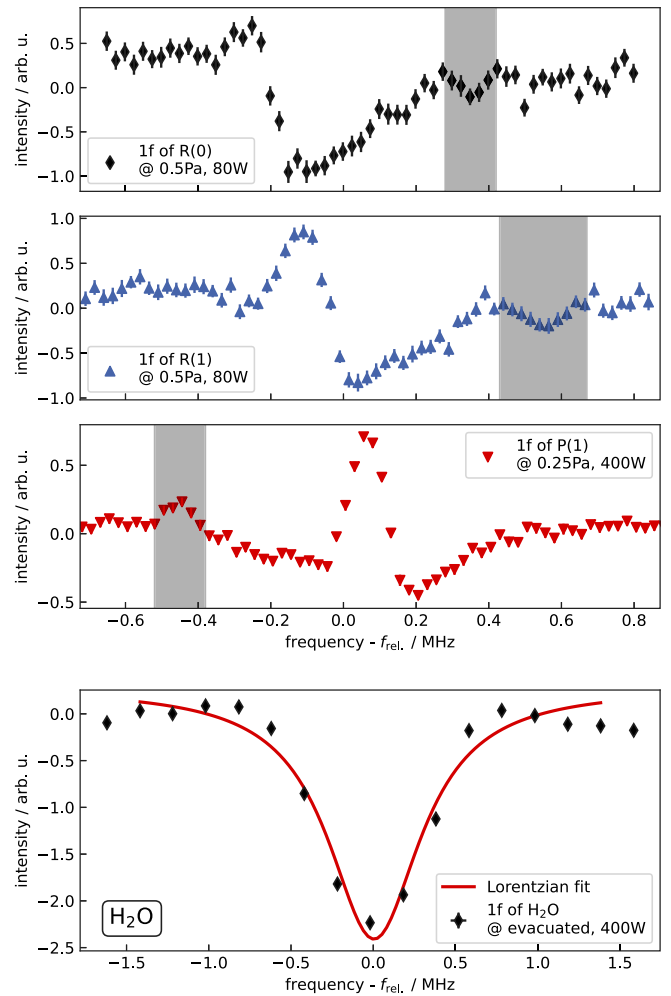


Fig. 8. Top: Spectral recordings of the R(0) ($J = 0 \rightarrow 1$), R(1) ($J = 1 \rightarrow 2$) and P(1) ($J = 1 \rightarrow 0$) transitions in the of $\nu = 0 \rightarrow 2$ overtone band of HT. Sample pressures relative to the constant ^3He background are indicated, as well as the intracavity circulating laser powers. The frequency scale is shifted for comparison of the lines. The weak resonance features inside the gray-shaded areas are connected to the isolated hyperfine components (see text). Bottom: Example of a single scan of a saturated water line used for adjustment and calibration of essential parameters. $f_{\text{rel.}}$ is an arbitrary frequency to shift the presented lines relative to each other. The line positions are presented in [26].

Similarly as in HD, the signal of the P(1) line appeared as a Lamb peak instead of a Lamb dip, for which some rationale was produced in the study of HD [24]. Again, for the P(1) line in HT, a single isolated hyperfine component was observed allowing to extract the rovibrational level energy. For further details on the NICE-OHMS spectroscopy of HT we refer to a previous Letter [26].

5. Conclusions

In this work, we present requirements, technical solutions and experiences of a NICE-OHMS setup developed to measure transitions in the radioactive molecular hydrogen isotopologue HT at different pressures, while keeping the background pressure low. Key component is the SAES St171 getter that enables reproducible provision of HT samples at different pressures in a closed setup through the temperature-dependent release of hydrogen isotopologues. In combination with a second getter, acting as a vacuum pump, the setup can be used under radiation-safe conditions using a tritiated hydrogen gas sample limited to an activity of 1 GBq.

In a dedicated study of the getter material it is demonstrated that the reversible ab- and desorption of H_2 , D_2 , T_2 and a H_2 :HT: T_2 mixture (with $H:T = 1:1$) using a SAES St171 getter is possible. In this study a similar volume and the same H_2 :HT: T_2 mixture is used as for the NICE-OHMS experiment, and it is shown that pressures of desorbed hydrogen up to 2.4 Pa are achievable. Some indications of isotope effects in the getter response are observed, but their influence on the composition of a gas mixture is found to be negligibly small.

During the ~ 300 h duration of the measurement campaign, focusing on the spectroscopic study of three transitions in HT about 120 gas samples were produced and no degradation of the getter/sample production performance is observed. Therefore, this experiment and the use of these getters can serve as a blueprint for similar experiments when small amounts of tritium (mixtures) at different pressures must be measured outside of licensed laboratories. While the spectroscopic study focused on the HT isotopologue, a similar study could be performed on the DT species that has equally strong dipole transitions. However the optics for the NICE-OHMS setup and lasers should be moved to a wavelength of 1825–1873 nm. With the recent observation of the overtone quadrupole transitions in the homonuclear H_2 molecule [53] it may be envisioned to extend the NICE-OHMS spectroscopy to T_2 at wavelengths in the range 2015–2065 nm.

CRedit authorship contribution statement

Valentin Hermann: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Conceptualization. **Benedict Rothmund:** Writing – review & editing, Visualization, Software, Investigation, Formal analysis. **Frank M.J. Cozijn:** Writing – review & editing, Software, Methodology, Investigation, Conceptualization. **Meissa L. Diouf:** Writing – review & editing, Software, Methodology, Investigation, Conceptualization. **Wim Ubachs:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. **Magnus Schlösser:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Wim Ubachs reports financial support was provided by Netherlands Organisation for Scientific Research. Magnus Schlösser reports financial support was provided by Baden-Württemberg Foundation. Wim Ubachs reports was provided by Laserlab-Europe. Co-author Meissa Libasse Diouf's new affiliation is the Department of Chemistry, University of Basel. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.vacuum.2024.113708>.

References

- [1] C.F. Cheng, J. Hussels, M. Niu, H.L. Bethlem, K.S.E. Eikema, E.J. Salumbides, W. Ubachs, M. Beyer, N. Hölsch, J.A. Agner, F. Merkt, L.G. Tao, S.M. Hu, C. Jungen, Dissociation energy of the hydrogen molecule at 10^{-9} accuracy, *Phys. Rev. Lett.* 121 (2018) 013001, URL <https://link.aps.org/doi/10.1103/PhysRevLett.121.013001>.
- [2] N. Hölsch, I. Doran, F. Merkt, J. Hussels, C.-F. Cheng, E.J. Salumbides, H.L. Bethlem, K.S.E. Eikema, M. Beyer, W. Ubachs, C. Jungen, Ionization and dissociation energies of HD and dipole-induced g/u -symmetry breaking, *Phys. Rev. A* 108 (2023) 022811, URL <https://link.aps.org/doi/10.1103/PhysRevA.108.022811>.
- [3] J. Hussels, N. Hölsch, C.-F. Cheng, E.J. Salumbides, H.L. Bethlem, K.S.E. Eikema, C. Jungen, M. Beyer, F. Merkt, W. Ubachs, Improved ionization and dissociation energies of the deuterium molecule, *Phys. Rev. A* 105 (2022) 022820, URL <https://link.aps.org/doi/10.1103/PhysRevA.105.022820>.
- [4] M. Puchalski, J. Komasa, P. Czachorowski, K. Pachucki, Complete a^6m corrections to the ground state of h_2 , *Phys. Rev. Lett.* 117 (2016) 263002, URL <https://link.aps.org/doi/10.1103/PhysRevLett.117.263002>.
- [5] M. Puchalski, J. Komasa, P. Czachorowski, K. Pachucki, Nonadiabatic QED correction to the dissociation energy of the hydrogen molecule, *Phys. Rev. Lett.* 122 (2019) 103003, URL <https://link.aps.org/doi/10.1103/PhysRevLett.122.103003>.
- [6] M. Puchalski, J. Komasa, A. Spyszkiewicz, K. Pachucki, Dissociation energy of molecular hydrogen isotopologues, *Phys. Rev. A* 100 (2019) 020503, URL <https://link.aps.org/doi/10.1103/PhysRevA.100.020503>.
- [7] E.J. Salumbides, J.C.J. Koelemeij, J. Komasa, K. Pachucki, K.S.E. Eikema, W. Ubachs, Bounds on fifth forces from precision measurements on molecules, *Phys. Rev. D* 87 (2013) 112008, URL <https://link.aps.org/doi/10.1103/PhysRevD.87.112008>.
- [8] E.J. Salumbides, A.N. Schellekens, B. Gato-Rivera, W. Ubachs, Constraints on extra dimensions from precision molecular spectroscopy, *New J. Phys.* 17 (3) (2015) 033015.
- [9] W. Hollik, M. Linster, M. Tabet, A study of new physics searches with tritium and similar molecules, *Eur. Phys. J. C* 80 (7) (2020) 661.
- [10] M. Schlösser, X. Zhao, M. Trivikram, W. Ubachs, E. Salumbides, CARS spectroscopy of the ($v = 0 \rightarrow 1$) band in t_2 , *J. Phys. B* 50 (21) (2017) 214004.
- [11] T.M. Trivikram, M. Schlösser, W. Ubachs, E. Salumbides, Relativistic and QED effects in the fundamental vibration of t_2 , *Phys. Rev. Lett.* 120 (16) (2018) 163002, URL <https://link.aps.org/doi/10.1103/PhysRevLett.120.163002>.
- [12] K.F. Lai, P. Czachorowski, M. Schlösser, M. Puchalski, J. Komasa, K. Pachucki, W. Ubachs, E.J. Salumbides, Precision tests of nonadiabatic perturbation theory with measurements on the DT molecule, *Phys. Rev. Res.* 1 (2019) 033124, URL <https://link.aps.org/doi/10.1103/PhysRevResearch.1.033124>.
- [13] K.-F. Lai, V. Hermann, T.M. Trivikram, M. Diouf, M. Schlösser, W. Ubachs, E.J. Salumbides, Precision measurement of the fundamental vibrational frequencies of tritium-bearing hydrogen molecules: T_2 , DT, HT, *Phys. Chem. Chem. Phys.* 22 (2020) 8973–8987.
- [14] D.K. Veirs, G.M. Rosenblatt, Raman line positions in molecular hydrogen: H_2 , HD, HT, D_2 , DT, and t_2 , *J. Mol. Spectrosc.* 121 (1987) 401–419, URL <https://www.sciencedirect.com/science/article/pii/0022285287900580>.
- [15] M.-C. Chuang, R.N. Zare, Rotation-vibration spectrum of HT: Line position measurements of the 1-0, 4-0, and 5-0 bands, *J. Mol. Spectrosc.* 121 (2) (1987) 380–400, URL <http://www.sciencedirect.com/science/article/pii/0022285287900579>.
- [16] L. Gianfrani, S.-M. Hu, W. Ubachs, Advances in cavity-enhanced methods for high precision molecular spectroscopy and test of fundamental physics, *Riv. Nuovo Cimento* 47 (2024) 229–298.
- [17] S. Kassi, A. Campargue, Electric quadrupole and dipole transitions of the first overtone band of HD by CRDS between 1.45 and 1.33 μm , *J. Mol. Spectrosc.* 267 (2011) 36–42.
- [18] E. Fasci, A. Castrillo, H. Dinesan, S. Gravina, L. Moretti, L. Gianfrani, Precision spectroscopy of HD at 1.38 μm , *Phys. Rev. A* 98 (2) (2018) 022516.
- [19] S. Kassi, C. Lauzin, J. Chaillot, A. Campargue, The (2–0) $r(0)$ and $r(1)$ transition frequencies of HD determined to a 10^{-10} relative accuracy by Doppler spectroscopy at 80 K, *Phys. Chem. Chem. Phys.* 24 (2022) 23164–23172.

- [20] L.-G. Tao, A.-W. Liu, K. Pachucki, J. Komasa, Y.R. Sun, J. Wang, S.-M. Hu, Toward a determination of the proton-electron mass ratio from the lamb-dip measurement of HD, *Phys. Rev. Lett.* 120 (2018) 153001.
- [21] F.M.J. Cozijn, P. Dupré, E.J. Salumbides, K.S.E. Eikema, W. Ubachs, Sub-Doppler frequency metrology in HD for tests of fundamental physics, *Phys. Rev. Lett.* 120 (2018) 153002, URL <https://link.aps.org/doi/10.1103/PhysRevLett.120.153002>.
- [22] M.L. Diouf, F.M.J. Cozijn, B. Darquié, E.J. Salumbides, W. Ubachs, Lamb-dips and lamb-peaks in the saturation spectrum of HD, *Opt. Lett.* 44 (19) (2019) 4733–4736.
- [23] T.-P. Hua, Y.R. Sun, S.-M. Hu, Dispersion-like lineshape observed in cavity-enhanced saturation spectroscopy of HD at 1.4 μm , *Opt. Lett.* 45 (17) (2020) 4863–4866.
- [24] M.L. Diouf, F.M.J. Cozijn, K.-F. Lai, E.J. Salumbides, W. Ubachs, Lamb-peak spectrum of the HD (2-0) p(1) line, *Phys. Rev. Res.* 2 (2) (2020) 023209, URL <https://link.aps.org/doi/10.1103/PhysRevResearch.2.023209>.
- [25] Y.N. Lv, A.W. Liu, Y. Tan, C.L. Hu, T.P. Hua, X.B. Zou, Y.R. Sun, C.-L. Zou, G.C. Guo, S.M. Hu, Fano-like resonance due to interference with distant transitions, *Phys. Rev. Lett.* 129 (2022) 163201, URL <https://link.aps.org/doi/10.1103/PhysRevLett.129.163201>.
- [26] F.M.J. Cozijn, M.L. Diouf, W. Ubachs, V. Hermann, M. Schlösser, Precision measurement of vibrational quanta in tritium hydride, *Phys. Rev. Lett.* 132 (11) (2024) 113002, URL <https://link.aps.org/doi/10.1103/PhysRevLett.132.113002>.
- [27] J. Ye, L.S. Ma, J. Hall, Sub-Doppler optical frequency reference at 1.064 μm by means of ultrasensitive cavity-enhanced frequency modulation spectroscopy of a C_2HD overtone transition, *Opt. Lett.* 21 (1996) 1000–1002.
- [28] O. Axner, W. Ma, A. Foltynowicz, Sub-Doppler dispersion and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy revised, *J. Opt. Soc. Am. B* 25 (2008) 1166–1177.
- [29] A. Foltynowicz, F.M. Schmidt, W. Ma, O. Axner, Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy: Current status and future potential, *Appl. Phys. B* 92 (2008) 313–326, URL <https://link.springer.com/article/10.1007/s00340-008-3126-z>.
- [30] O. Axner, P. Ehlers, A. Foltynowicz, I. Silander, J. Wang, NICE-ohms frequency modulation cavity-enhanced spectroscopy: principles and performance, in: G. Gagliardi, H.-P. Loock (Eds.), *Cavity-Enhanced Spectroscopy and Sensing*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2014, pp. 211–251.
- [31] K. Pachucki, J. Komasa, Electric dipole rovibrational transitions in the HD molecule, *Phys. Rev. A* 78 (2008) 052503, URL <https://link.aps.org/doi/10.1103/PhysRevA.78.052503>.
- [32] M. Sturm, F. Priester, M. Röllig, C. Röttle, A. Marsteller, D. Hillesheimer, L. Bornschein, B. Bornschein, R. Gröfle, S. Welte, Kilogram scale throughput performance of the KATRIN tritium handling system, *Fusion Eng. Des.* 170 (2021) 112507, URL <https://www.sciencedirect.com/science/article/pii/S0920379621002830>.
- [33] D. Díaz Barrero, T.L. Le, S. Niemes, S. Welte, M. Schlösser, B. Bornschein, H.H. Telle, Generation and analysis of tritium-substituted methane, *Fusion Sci. Technol.* 80 (3–4) (2024) 530–539.
- [34] F. Schmidt-Bleek, F.S. Rowland, Recoil reactions of tritium with organic compounds, *Angew. Chem. Int. Ed. Engl.* 3 (12) (1964) 769–776.
- [35] Y.N. Tang, F.S. Rowland, Recoil tritium reaction: Ring opening and alkyl replacement in substituted cyclopropanes, *J. Phys. Chem.* 69 (12) (1965) 4297–4304.
- [36] P.J. Kuntz, E.M. Nemeth, J.C. Polanyi, W.H. Wong, Distribution of reaction products. VI. Hot-atom reactions, $\text{T} + \text{HR}$, *J. Chem. Phys.* 52 (9) (1970) 4654–4674.
- [37] A. Campargue, S. Kassi, K. Pachucki, J. Komasa, The absorption spectrum of H_2 : CRDS measurements of the (2-0) band, review of the literature data and accurate ab initio line list up to 35000 cm^{-1} , *Phys. Chem. Chem. Phys.* 14 (2012) 802–815.
- [38] D. James, G. Morgan, Evaluation of getters for methane and ammonia decomposition, *Fusion Eng. Des.* 133 (2018) 1–5.
- [39] G. Ana, O. Balteanu, I. Cristescu, R. Ana, Concept for HCPB TER using non-evaporable getters for tritium recovery, *Fusion Eng. Des.* 201 (2024) 114291, URL <https://www.sciencedirect.com/science/article/pii/S0920379624001443>.
- [40] A. Santucci, L. Farina, S. Tosti, A. Frattolillo, Novel non-evaporable getter materials and their possible use in fusion application for tritium recovery, *Molecules* 25 (2020).
- [41] A. Ashtari Esfahani, S. Böser, N. Buzinsky, M.C. Carmona-Benitez, C. Claessens, L. de Viveiros, P.J. Doe, M. Ferti, J.A. Formaggio, J.K. Gaison, L. Gladstone, M. Grando, M. Guigue, J. Hartse, K.M. Heeger, X. Huyan, J. Johnston, A.M. Jones, K. Kazkaz, B.H. LaRoque, M. Li, A. Lindman, E. Machado, A. Marsteller, C. Matthé, R. Mohiuddin, B. Monreal, R. Mueller, J.A. Nikkel, E. Novitski, N.S. Oblath, J.I. Peña, W. Pettus, R. Reimann, R.G.H. Robertson, D. Rosa De Jesús, G. Rybka, L. Saldaña, M. Schram, P.L. Slocum, J. Stachurska, Y.-H. Sun, P.T. Surukuchi, J.R. Tedeschi, A.B. Telles, F. Thomas, M. Thomas, L.A. Thorne, T. Thümmel, L. Tvrznikova, W. Van De Pontseele, B.A. VanDevender, J. Weintraub, T.E. Weiss, T. Wendler, A. Young, E. Zayas, A. Ziegler, Project 8 Collaboration Collaboration, Tritium beta spectrum measurement and neutrino mass limit from cyclotron radiation emission spectroscopy, *Phys. Rev. Lett.* 131 (2023) 102502, URL <https://link.aps.org/doi/10.1103/PhysRevLett.131.102502>.
- [42] B.K. Das, R. Das, R. Verma, R. Shukla, A. Sharma, Improvement of deuterium emission by St 172 NEG pump in a sealed off vacuum device, *Vacuum* 181 (2020) 109743.
- [43] Y. Yamamoto, H. Konda, Y. Matsuyama, H. Osawa, M. Ohnishi, Characteristics of gas mixture supply/pressure control using non-evaporable getters in a discharge-type fusion neutron source, *Fusion Sci. Technol.* 72 (2017) 773–779.
- [44] S. Niemes, H.H. Telle, B. Bornschein, L. Fasselt, R. Gröfle, F. Priester, M. Schlösser, M. Sturm, S. Welte, G. Zeller, Accurate reference gas mixtures containing tritiated molecules: Their production and Raman-based analysis, *Sensors* 21 (18) (2021) URL <https://www.mdpi.com/1424-8220/21/18/6170>.
- [45] F.M.J. Cozijn, M.L. Diouf, V. Hermann, E.J. Salumbides, M. Schlösser, W. Ubachs, Rotational level spacings in HD from vibrational saturation spectroscopy, *Phys. Rev. A* 105 (6) (2022) 062823.
- [46] C. Boffito, B. Ferrario, D. Martelli, Equilibrium pressures of h_2 and d_2 for different getter materials and the effect of CO impurities, *J. Vacuum Sci. Technol. A* 1 (1983) 1279–1282.
- [47] R.J. Knize, J.L. Cecchi, H.F. Dylla, Measurement of h_2 , d_2 solubilities in Zr–Al, *J. Vacuum Sci. Technol.* 20 (4) (1982) 1135–1137.
- [48] K. Ichimura, N. Inoue, K. Watanabe, T. Takeuchi, Absorption and desorption of hydrogen, deuterium, and tritium for Zr–V–Fe getter, *J. Vacuum Sci. Technol. A* 2 (3) (1984) 1341–1347.
- [49] W.M. Jones, Thermodynamic functions for tritium and tritium hydride. The equilibrium of tritium and hydrogen with tritium hydride. The dissociation of tritium and tritium hydride, *J. Chem. Phys.* 16 (11) (1948) 1077–1081.
- [50] L.L. Lucas, M.P. Unterwieser, Comprehensive review and critical evaluation of the half-life of tritium, *J. Res. Nat. Inst. Stand. Tech.* 105 (4) (2000) 541, URL <https://nvlpubs.nist.gov/nistpubs/jres/105/4/j54luc2.pdf>.
- [51] T. Schober, K. Farrell, Helium bubbles in α -Ti and Ti tritide arising from tritium decay: A TEM study, *J. Nucl. Mater.* 168 (1) (1989) 171–177, URL <https://www.sciencedirect.com/science/article/pii/0022311589905795>.
- [52] F.M.J. Cozijn, M.L. Diouf, W. Ubachs, Saturation spectroscopy of $\text{r}(0)$, $\text{r}(2)$ and $\text{p}(2)$ lines in the (2-0) band of HD, *Eur. Phys. J. D* 76 (11) (2022) 220, URL <https://link.springer.com/article/10.1140/epjd/s10053-022-00552-x>.
- [53] F.M.J. Cozijn, M.L. Diouf, W. Ubachs, Lamb dip of a quadrupole transition in h_2 , *Phys. Rev. Lett.* 131 (2023) 073001, URL <https://link.aps.org/doi/10.1103/PhysRevLett.131.073001>.