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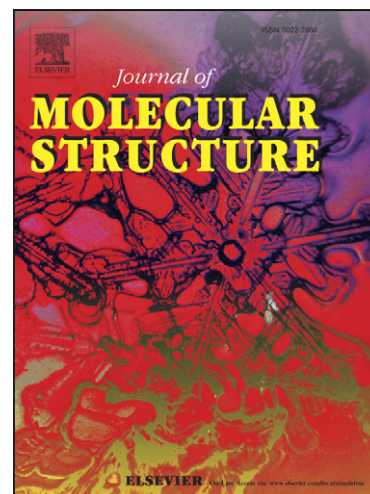
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Accurate Calibration of the Laser Raman System for the Karlsruhe Tritium Neutrino Experiment

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Abstract

The Karlsruhe Tritium Neutrino (KATRIN) experiment aims to measure the neutrino mass via high-precision electron spectroscopy of the tritium β-decay with a sensitivity of $m_\nu = 200 \, \mathrm{meV/c^2} \, (90\% \, \mathrm{C.L.})$. This can only be achieved if systematic uncertainties are minimized. An important parameter is the isotopic composition of the tritium gas used as the gaseous β-electron source, which is measured inline by Raman spectroscopy. The KATRIN experiment requires a measurement trueness of better than 10% of said composition; to achieve this, accurate calibration of the Raman system for all hydrogen isotopologues (H_2, HD, D_2, HT, DT, T_2) is required. Here we present two independent calibration methods, namely (i) a gas sampling technique, which promises high accuracy, but which is difficult to apply to tritiated species; and (ii) an approach via theoretical Raman signals (theoretical intensities plus spectral sensitivity), which in principle includes all six isotopologues. For the latter method we incorporated *ab-initio* off-diagonal matrix elements of the polarizability from the literature; these have been verified by depolarization measurements. The system's spectral sensitivity was determined by a NIST-traceable SRM2242 luminescence standard. Both methods exhibited their individual merits and difficulties, but in cross calibration proved to be successful: a comparison for the non-radioactive

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isotopologues (H_2, HD, D_2) yielded agreement to better than 2% for the relative Raman response function. This is within the estimated (dominant) uncertainty of the theoretical Raman signal approach of about 3%. Therefore, one can be confident that, when using this approach, the trueness requirement of 10% for the KATRIN-relevant species (T_2, DT, D_2 and HT) will in all likelihood be exceeded.

1. Introduction

The **KA**rlsruhe **TRI**tium **N**eutrino experiment (KATRIN) will measure the neutrino mass with a sensitivity of $m_\nu = 200\,\text{meV}/c^2$ (90% C.L.). The methodology is based on high-precision electron spectroscopy of the tritium β-decay near its kinematic endpoint at about 18.6 keV [1]. The systematic uncertainty of this measurement is influenced by several parameters; of particular importance is the precise knowledge of the purity of the tritium gas which is used as the gaseous β-electron source [2].

While one strives for the highest possible tritium purity, due to the way it is produced the gas is always composed of a mixture of T_2 ($> 90\%$), DT ($< 10\%$), and traces of HT, D_2, HD and H_2. In a first instance, the gas composition of the gaseous β-electron source influences the activity and thus the count-rate in the β-spectrum. For this, only relative changes are of interest. However, the composition has to be monitored continuously in time intervals of less than 250 s and with a measurement precision of at least 0.1% [1]. The operating pressure is in the range $150 - 200$ mbar [2]. The feasibility of these requirements has been demonstrated using laser Raman spectroscopy (LARA) [3].

It has to be noted that the tritium-containing isotopologues (T_2, DT, HT) exhibit different final-state distributions of ro-vibrational excitations of the corresponding daughter nuclei (^{3}HeT, ^{3}HeD, ^{3}HeH), which in turn influence the energy of the β-electrons in the region of interest [4]. To account for this in the

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KATRIN experiment, tracing the relative changes in the tritium gas composition is not any longer sufficient, but now the trueness[1] of the LARA measurements is of crucial importance. According to simulations, the trueness should be at least better than 10% [6] for a period of at least 60 days, which is equivalent to one single KATRIN neutrino measurement run. To gauge the actual trueness of the LARA measurement an accurate intensity calibration of the LARA system is necessary. In this context calibration means that the relative Raman intensities (as shown in a typical Raman spectrum below in Fig. 1) can be converted into absolute component concentrations.

In this paper we present a calibration strategy for the LARA system of the KATRIN experiment which consists of two approaches, and we demonstrate their successful application to calibrating our system, together with a detailed analysis of the systematic uncertainties associated with the two methods. Finally, both methods are compared to each other. It should be pointed out, that the methods and results presented within this publication are not limited to the application in the KATRIN experiment. A similar accountancy task is found within the fuel cycle of future fusion reactors [7]. Here, the requirements for the trueness are of the order of 1% [8]. In general, the calibration methods presented are applicable to most gas analysis systems, but in particular to those which include species which cannot be obtained by simple gas mixing.

2. Experimental system and procedures

The Raman system employed in this work is essentially the system described in Sturm *et al*, [9] with the light collection and detection system comprising

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[1]The terminology of "precision", "trueness" and "accuracy" can be found in a publication by the Joint Committee for Guides in Metrology [5]. In short: **Precision** is the reproducibility of a measurement (spread of single values around the mean value); **trueness** is the deviation of the mean value to the true value; and the deviation of a single measurement value to the true value is the **accuracy**. Thus, if a measurement is both "precise" and "true", it is called "accurate".
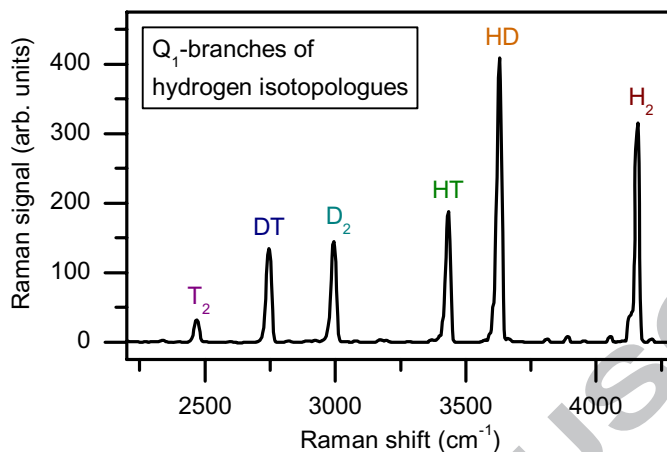
Figure 1: Typical Raman spectrum of a gas mixture containing all six hydrogen isotopologues. All minor, unassigned lines between the Q_1 branches are S_1 and O_1 lines of the six hydrogen isotopologues.

optics for imaging the Raman excitation volume onto an optical fibre bundle, optics to transfer the fibre bundle output through a razor-edge Rayleigh filter onto the spectrometer slit, a Czerny-Turner spectrograph and a CCD 2D-array detector. Some modifications were made to that early system version, namely (i) a retro-reflecting mirror for nearly doubled laser intensity was inserted; (ii) the plano-convex lenses in the light collection path were replaced by two 2"-diameter achromatic lenses with $f = 75$ mm, to reduce chromatic aberrations; and (iii) the PI-Acton HTS spectrometer was replaced by a PI-Acton SP2150 unit ($f = 150$ mm, 600 gr/mm). In addition, a linear polarizer was introduced between the two collection achromats, which ensures that polarization effects in the light collection and detection system (associated with the fibre bundle, edge filter, grating, CCD-detector) do not have to be considered. A typical spectrum acquired with this Raman system is shown in Fig. 1; all six hydrogen isotopologues present in the particular gas mixture can be identified.

From such a spectrum the Raman signal amplitude, S_x, of a certain isotopologue x can be obtained. It is related to the number of molecules in the sample, N_x. A system-dependent response function, R_x, provides the proportionality

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between the Raman signal and the particle number,

$$S_x = R_x \cdot N_x. \tag{1}$$

Note that in general the area under a certain Q_1-branch peak is taken as the total Raman signal. Relative Raman signal amplitudes, $S_{x,\mathrm{rel}}$, are obtained by normalizing the individual signal amplitudes to the sum of the signal amplitudes of all isotopologues in the sample. Accordingly, equation (1) is modified to

$$S_{x,\mathrm{rel}} = R_x \cdot N_x / (\sum_i R_i \cdot N_i). \tag{2}$$

The objective of a calibration is to determine values for R_x for any of the constituents in the sampled gas, in our case all hydrogen isotopologues. For easier comparison of the individual components it is useful to normalize the absolute response functions by the mean of all response functions, arriving at the relative response functions, $R_{x,\mathrm{rel}}$,

$$R_{x,\mathrm{rel}} = R_x / R_{\mathrm{mean}} = n \cdot R_x / \sum_{i=1}^{n} R_i \ . \tag{3}$$

In this paper we have contemplated three possible approaches to achieve an accurate calibration of our Raman system, namely (i) to use reference method(s) for cross-calibration; (ii) to measure spectra of known calibration samples; and (iii) to employ literature or theoretical values for the Raman cross-sections in combination with the measurement of the system's spectral sensitivity.

With the respect to the first, there is hardly any reference method available for the compositional measurement of tritium mixtures, which provides sufficient trueness [10, 7]. Certainly, at the Tritium Laboratory Karlsruhe (TLK), a laboratory with renowned expertise in tritium analytics, no system is currently available to provide the required trueness.

As for the second approach, the generation and use of accurate samples is a widely used technique; specifically, such samples are very accurate in solid or liquid form, especially if they are produced by gravimetric preparation. However, in general, to provide accurate, homogeneous gas mixtures is substantially

more complicated, as described in the ISO standard 6142 [11]. When dealing with tritium gas mixtures additional difficulties are encountered: (a) restricted handling of tritium due to safety regulations; (b) limited purity of the desired T_2 constituent; and (c) radio-chemical and exchange reactions with other species and the walls (Souers [12] and references therein).

With regard to the third approach, experimentally verified literature values for the cross-sections of the radioactive hydrogen isotopologues T_2, DT and HT are not available.

It should be noted that a theoretical concept allows one to predict so-called "theoretical intensities" for all six hydrogen isotopologues [13]. However, since no trueness of these values is discussed within said publication, the question arises as to which level of confidence one can rely on these theoretical values.

Therefore, the solution for a successful calibration can only be a combination of the two latter approaches (ii) and (iii), i.e. to use theory values and the system's (measured) spectral sensitivity to arrive at the aforementioned relative response functions, $R_{x,\mathrm{rel}}$. These are verified by preparing calibration samples of the non-radioactive isotopologues H_2, HD and D_2. The restriction to non-tritiated species was necessary since a tritium-certified mixing system with sufficient accuracy was not available at the time of these calibration measurements. A successful verification of the relative response functions for the three non-radioactive isotopologues should then provide sufficient confidence to deduce the relative response functions of the tritiated isotopologues without direct experimental verification.

Of course, in a future step, the sampling method may be extended to cover all isotopologues to allow for a complete comparison. While seemingly straightforward in its concept, this calibration procedure has to fulfill certain requirements. Firstly, the approach needs a method and an apparatus to obtain highly accurate H_2, D_2 and HD samples. Secondly, it is necessary to generate appropriate theoretical intensity values and compare them with accurately measured ones, so that a high level of confidence can be placed in the theoretical values. Finally, an accurate method for measuring the system's spectral sensitivity is needed.

Below the realization of both approaches (ii) and (iii) is discussed, together with the estimated systematic uncertainties of each.

3. Results

3.1. Approach I: Calibration based on accurate gas samples

As stated above, the calibration with gas samples only includes the three non-radioactive isotopologues H_2, HD and D_2. The method and the experimental device are briefly introduced here; a full description and discussion can be found in a separate publication[2]. One should recall that equation (2) represents the relation between the relative Raman signal amplitudes $S_{x,\mathrm{rel}}$ from the Raman measurements and the isotopologue compositions N_x. Thus, if the latter is known from the sample mixing, then R_x can be obtained. The basic principle behind our accurate gas mixing is that two gas vessels of the same volume are filled with pure H_2 and D_2 gas at precisely determined pressures. The ratio of the pressures is then automatically equal to the ratio of the number densities in the mixtures once both vessels are connected to each other. The direct extension of this calibration method to HD is not possible, since in general HD is not commercially available in a high purity [14]. However, by cycling the mixed H_2/D_2 gas through a catalyst reactor (0.5% Pt on 1/16" Al_2O_3 from Alfa Aesar), HD is produced in the equilibrium exchange reaction $H_2 + D_2 \rightleftharpoons 2HD$ (with the equilibrium constant $K = [HD]^2/([H_2][D_2])$) during the calibration procedure itself. Said gas mixing system, including the catalyst reactor, has been set up at TLK; its schematic layout is shown in Fig. 2. The construction and functionality of the system as well as the measurement results are described elsewhere[2]. Using this system, sets of measurements with different initial concentrations of H_2 and D_2 were performed. The simultaneous fit to the relative Raman signal amplitudes $S_{H_2,\mathrm{rel}}$, $S_{D_2,\mathrm{rel}}$ and $S_{HD,\mathrm{rel}}$ generates the related calibration functions

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[2]Description and data are part of a manuscript submitted to *Anal. Chem.* but as yet unpublished, therefore a preview on the results in given in the "Supplementary material".
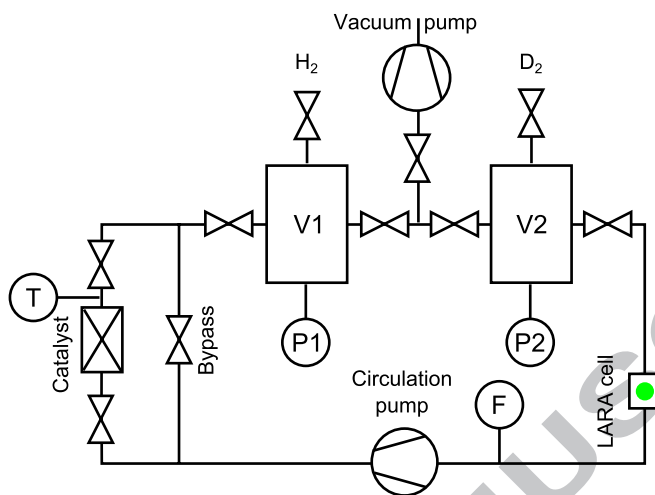
Figure 2: Simplified flow diagram of the HYdrogen Deuterium Equilibration loop (HYDE). V_i = calibrated pressure vessels; P_i = pressure gauges; F = flow controller; T = thermocouple.

$R_{\mathrm{H_2}}$, $R_{\mathrm{D_2}}$ and R_{HD}, without the necessity for accurate control of the reaction temperature, which defines the equilibrium constant $K(T)$. The measurement points and resulting fit curves from such a calibration set are shown in Fig. 3. Note, that (i) the error bars are smaller than the symbols in the plot; and that (ii) measurements at initial hydrogen mole fractions of $y_{i,\mathrm{H_2}} = 0.2$ and $y_{i,\mathrm{H_2}} = 0.8$ have been performed twice to test the reproducibility of the procedure. The related repeat data points overlap to such an extent that no data scatter is noticeable on the scale of the symbols. The full fitting results are tabulated in the comparison section further below.

3.2. Approach II: Calibration based on theoretical intensities and spectral sensitivity

Other than in the sampling approach described in Section 3.1, in the second approach all six hydrogen isotopologues are in principle covered. Equation (1) needs to be written in a slightly different form: The Raman signal amplitude is now given as the product of the spectral sensitivity, $\eta(\lambda_s)$, and theoretical Raman intensity, $I_{\mathrm{Raman,x}}(\lambda_s, N_x)$, and will thus be called "theoretical Raman
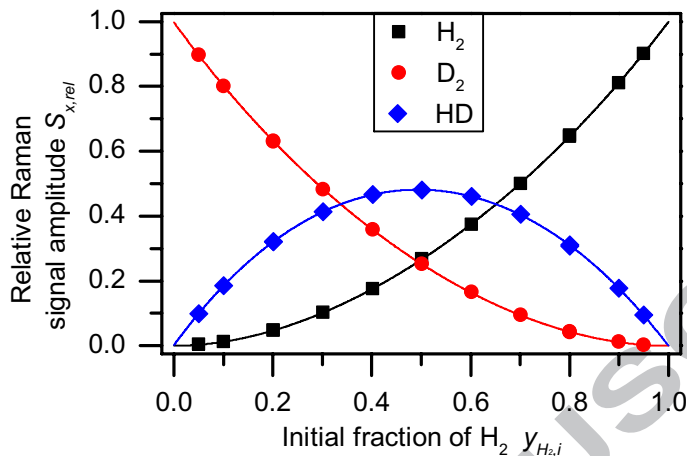
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Figure 3: Fitting of the HYDE data at a catalyst temperature of 25 °C. Horizontal axis: mole fraction $y_{i,\mathrm{H_2}}$ of H_2 before the equilibration of the mixture. Vertical axis: measured relative Raman intensities of the three components. Legend: symbols - measurement points; lines - fit curves. For further details see main text.

signal amplitude" for the remainder of this publication:

$$S_x = \eta(\lambda_s) \cdot I_{\mathrm{Raman,x}}(\lambda_s, N_x) \tag{4}$$

$$= \eta(\lambda_s) \cdot C \cdot \lambda_0^{-1} \cdot \lambda_s^{-3} \cdot \Phi_x \cdot \Im \cdot N_x. \tag{5}$$

Here, C is a proportionality constant, λ_0 is the wavelength of excitation laser, λ_s is the wavelength of the Raman scattered light[3], Φ_x is the molecule dependent line strength function, and $\Im$ is the irradiance. It should be noted that equation (5) is a simplification; it is assumed that the signal only consists of a single monochromatic line. In reality, the Q_1-branches used in the calibration consist of a series of unresolved individual lines associated with the different initial rotational states with quantum number J (this feature is evident from the "non-Gaussian" shape in the example spectrum in Fig. 1). The population of these initial states can be calculated from the Boltzmann distribution and the nuclear

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[3]The wavelength dependence is often given as λ_s^{-4} in the literature. McCreery discusses in this reference [15] that this term is valid for intensity measurements in Watts/s, whereas the λ_s^{-3} term is valid for measurements in photons/s (e.g. as in a CCD detector).

spin degeneracy g_N [4]. Thus, for the actual case encountered in our calibration measurements equation (5) has to take this multi-line scenario into account, and needs to be modified to

$$S_x = \underbrace{C \cdot \lambda_0^{-1} \cdot \Im}_{\text{const.}} \cdot N_x \cdot$$

$$\underbrace{\sum_J \left(\eta(\lambda_{s,J}) \cdot \lambda_{s,J}^{-3} \Phi_{x,J} (2J+1) g_N \exp\left(-\frac{\tilde{F}(J)hc}{kT} \right) / Q \right)}_{R'_x} \qquad (6)$$

with the molecular partition function Q [16]

$$Q = \sum_J \left((2J+1) g_N \exp\left(-\frac{\tilde{F}(J)hc}{kT} \right) \right) . \qquad (7)$$

This description of the Raman signal in relation to particle numbers is now similar to equation (1) again. Note that, since the first three factors are constant, they will cancel out when calculating the relative response functions (see equation (3)). Therefore, only the functions R'_x are of interest, which will be discussed in detail below.

3.2.1. Raman intensities

The contribution of R'_x in equation (6) is related to theoretical Raman intensities,

$$R'_x = \sum_J \left(\eta(\lambda_{s,J}) \cdot \lambda_{s,J}^{-3} \Phi_{x,J} (2J+1) g_N \exp\left(-\frac{\tilde{F}(J)hc}{kT} \right) / Q \right) \qquad (8)$$

where $\tilde{F}(J)$ represents the rotational term energies. The $\tilde{F}(J)$-values can be obtained from the accurate measurement of the line positions.[17] The term $\Phi_{x,J}$ is the line strength function, which is a function of the tensor invariants a and

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[4]For even J: ($g_N = 1$ for H_2, T_2; $g_N = 2$ for D_2); For odd J: ($g_N = 3$ for H_2, T_2; $g_N = 1$ for D_2). The heteronuclear molecules (HD, HT, DT) have no nuclear spin degeneracy and thus $g_N = 1$.

γ, i.e. the isotropic and anisotropic polarizabilities, respectively. [16] As indicated by the symbol, these tensor invariants are individually different for each rotational J-level of the different isotopologues x. These values can be obtained from *ab initio* quantum calculations. In the 1980s Schwartz and LeRoy calculated the potentials and tensor invariants for all six hydrogen isotopologues, for the laser excitation wavelength $\lambda_0 = 488\,\text{nm}$. [13] For our particular case here, i.e. Raman excitation based on $532\,\text{nm}$ lasers (Nd:YAG / Nd:VO$_4$), the tensor invariants a and γ were recalculated for this specific wavelength. [18] However, since no trueness of these values is discussed in LeRoy's publications, the question arises as to which level of confidence one can rely on these theoretical values. This is associated with the fact that no uncertainties are published for said calculations. Therefore, we conducted an experiment for their verification. In that context, direct access to the individual tensor invariants is normally difficult; however, verification is feasible via depolarization ratio measurements [19]. Our methodology for accurately measuring and analyzing the depolarization ratios is discussed elsewhere.[20] There we describe the development of methods to correct for the non-zero collection angle and depolarization effects occurring in the Raman cell windows. Recently, we measured the depolarization ratios of the Q_1-lines ($J" = 0$ to $J" > 3$) of all six hydrogen isotopologues[5]. Our experimental values agree with the theoretically derived values, based on the calculations of LeRoy, [18] to within 5%. Using error propagation[6] it can be shown that the relative uncertainty of the depolarization ratio is about equal to the relative uncertainty of the line strength function. However, it should be made clear at this point that the aforementioned errors do not necessarily express the true uncertainty of the values, as obtained from the theory. Rather, they define the degree of confidence we currently place in the theoretical data.

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[5]Results are part of a publication to be published in *J. Raman Spectrosc.* Also see the "Supplementary material".

[6]Given in detail within the "Supplementary material" of this publication.

3.2.2. Spectral sensitivity

Broadly speaking, the spectral sensitivity is the relative efficiency for the detection of photons in a light acquisition system, as a function of wavelength. Foremost, it is determined by the wavelength-dependent responses of the diffraction grating of the spectrograph and the CCD-detector. However, in general the spectral sensitivity becomes even more complex because of further components in the complete acquisition system (like e.g. optical fibre bundle, AR-coated lenses, edge filters, etc.); all of them exhibit their own polarization dependence. Therefore, as already mentioned in Section 2 above, a linear polarizer is introduced at the front end of the light collection system to minimize the influence of the latter components on the depolarization ratio measurements. An external light source is needed for the calibration of the system's spectral sensitivity. A common approach for calibrating the spectral sensitivity is the use of a certified blackbody radiator. However, commercial blackbody radiators with small uncertainties (e.g. $< 2\%$) are not only relatively expensive but also have a rather short certified lifetime, with often only about 50 hours (note that in general already ~ 30 minutes are needed each time of use before the output is stabilized). A major disadvantage of such sources is that the volume/area of light generation normally differs considerably from the scattering region, which produces the Raman light. In our case, the Raman excitation volume can be approximated by a cylinder of diameter $d \approx 150\,\mu$m, with a length of some millimeters. Blackbody radiators are by and large based on tungsten filaments of much larger size and often non-uniform shape. Measurements performed within the framework of our current research program showed that the exact position of the light, be it the Raman light or the calibration light, is crucial for the accuracy of the measured data, due to chromatic aberrations throughout the chain of optics. The solution employed in this work overcomes all above-mentioned difficulties, i.e. the calibration device (i) has a longer lifetime; (ii) provides and acts as a nearly perfect imitation of the Raman scattered light region; and (iii) is substantially cheaper. The device in question is a SRM2242 Raman standard,

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manufactured, certified and distributed by NIST (for more details see the corresponding NIST certificate for Standard Reference Material 2242 and Choquette *et al* [21]). Note that this SRM2242 luminescence standard is designated for the use in backscattering Raman experiments (e.g. micro-Raman measurement devices). Therefore, the use of this device in a $90\,^\circ$-configuration constitutes a non-standard operation condition; however, in extensive checks we confirmed that the spectral distribution function remained valid (see below). The Raman shift range covered by the NIST-certified polynomial is $150 - 4000\,\mathrm{cm}^{-1}$; the $\pm 2\sigma$ calibration uncertainties are tabulated over the full range. According to the certification protocol, the relative uncertainty is less than 1% for the Q_1-branch lines of the isotopologues of relevancy to the KATRIN measurements, i.e. T_2, DT, D_2 and HT. The Q_1-branch of H_2 (at $\sim 4200\,\mathrm{cm}^{-1}$), which is included in our analysis for completeness, lies just outside the certified region. NIST provided an extended dataset up to $7000\,\mathrm{cm}^{-1}$, yet without certification of that extended range. The calibrated spectral sensitivity of our system is shown in Fig. 4. The ripple in the data traces can be associated with the transmission function of the razor-edge Raman filter for rejection of the Rayleigh scattered light (see the *Semrock* LP03-532RU-25 datasheet). Perfect mimicking of the Raman light excitation region can be established using a simple setup as shown in Fig. 5. The mount for the SRM2242 standard is attached to the same type of dovetail, which is used for mounting the Raman cell. Thus, the Raman cell can be removed and replaced by the calibration standard, with very high spatial reproducibility. The following systematic investigation have been performed in order to verify whether operating the SRM2242 standard in non-backscatter geometry is influenced systematically by the following effects: (i) changes in the incident excitation laser polarization; (ii) temperature variation; (iii) variation in laser power; and (iv) influence of the cell windows in the direction of the light collection. It could be shown that the variations associated with these effects are within the range of the certified $\pm 2\sigma$ standard deviation. The detailed results of this investigation will be subject of a future publication.
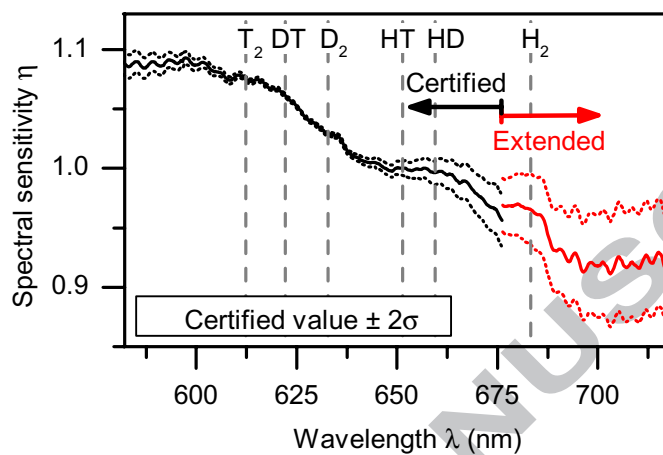
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Figure 4: Spectral sensitivity of the detection system, measured using the SRM2242 NIST standard. Note the discontinuity at the transition from the certified to the extended range (extended data also provided by NIST).
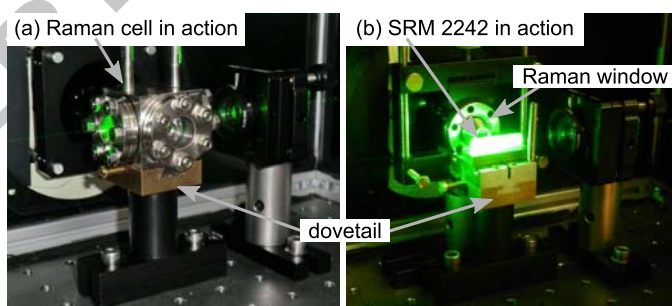

Figure 5: Operation of the LARA system with (a) Raman cell, or (b) SRM 2242 luminescence reference standard.

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Table 1: Raman response functions based on theoretical Raman signal amplitudes, and the related uncertainties. All R'_x have been normalized so that $R'_{H_2} = 1$. For the meaning of $\Delta R'_{\text{theo}}$ and $\Delta R'_{\text{sens}}$ see the main text.

Isotopologue	R'_x	$\Delta R'_{\text{theo}}$ (%)	$\Delta R'_{\text{sens}}$ (%)	$\Delta R'_{\text{tot}}$ (%)
H_2	1.000	2.9	2.7	3.9
HD	0.981	3.0	0.9	3.1
HT	0.960	3.1	0.5	3.2
D_2	0.925	3.4	0.2	3.4
DT	0.914	3.7	0.1	3.7
T_2	0.866	3.9	0.2	3.9

3.2.3. Resulting theoretical Raman signal amplitudes and uncertainties

In Table 1 the system response values, R'_x, derived from the theoretical Raman signal amplitudes are tabulated, together with the estimated uncertainties. The uncertainties are split into two terms, namely (i) the contribution $\Delta R'_{\text{theo}}$, which is associated with the confidence we place in the theoretical values, as obtained from the depolarization measurements; and (ii) the contribution $\Delta R'_{\text{sens}}$, which stems from the calibration of the spectral sensitivity. The quadratic sum of both uncertainty contributions, constitutes the overall uncertainty, $\Delta R'_{\text{tot}}$.

As can be seen, the overall uncertainty in the response function, as summarized in Table 1, is well below 5%. However, it is obvious that the confidence in the "theory" (which includes the depolarization measurements undertaken to cross-check the *ab initio* line strengths) currently dominates the total error estimation, with the exception of H_2. Its $\Delta R'_{\text{sens}}$ error is comparatively higher, since the required spectral calibration data are out of the certified range provided by NIST.

3.3. Comparison

The two calibration approaches have been performed for H_2, D_2 and HD. The results from both techniques are now compared to ascertain whether they

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Table 2: Comparison of response functions as obtained by the two approaches discussed in this publication. Note that the $R_{x,\mathrm{rel}}$-representation offers better means for comparing the two than the R'_x-representation, for which the data are normalized to $R'_{\mathrm{H}_2} = 1$ (cf. Table 1).

| | Theoretical Raman signals | | | HYDE measurements | | Difference |
	Value	Δ_{sens} (%)	Δ_{tot} (%)	Value	Δ_{tot} (%)	Theo. Ram. sign.−HYDE (%)
$R_{\mathrm{H}_2,\mathrm{rel}}$	1.032	1.9	3.0	1.013	< 0.5	1.9
$R_{\mathrm{D}_2,\mathrm{rel}}$	0.955	2.1	2.9	0.969	< 0.5	-1.5
$R_{\mathrm{HD},\mathrm{rel}}$	1.013	2.0	2.7	1.018	< 0.5	-0.5
$R_{\mathrm{H}_2}/R_{\mathrm{D}_2}$	1.081	2.8	5.2	1.045	< 0.6	3.4
$R_{\mathrm{HD}}/R_{\mathrm{D}_2}$	1.061	0.9	4.9	1.050	< 0.6	1.0

agree within the estimated uncertainties. The related data are collated in Table 2. Here we compare the relative response functions, as defined in equation (3), and ratios of two response functions R_i/R_j, where the indices relate to different isotopologues. The uncertainties, Δ, are obtained from error propagation through the relative response functions. Note, that in the formation of relative response functions, the response function for H_2 with its large uncertainty (associated with the larger errors in the uncertified spectral sensitivity) dominates the uncertainties of the $R_{x,\mathrm{rel}}$ functions.

The uncertainties of the response function values, obtained using the gas sample method, are well below 1%. A detailed discussion of the error estimation for this method can be found elsewhere[2].

The table entries show that the relative response function values, $R_{x,\mathrm{rel}}$, and the response function ratios, R_i/R_j, obtained from the two approaches agree to better than 2%. The only exception is encountered for the $R_{\mathrm{H}_2}/R_{\mathrm{D}_2}$ ratio, which has a difference of 3.4%. As pointed out above, this is most likely caused by the higher uncertainty in the calibration of the spectral sensitivity in the wavelength range of H_2. Nevertheless, the overall agreement for both approaches is well within the bounds given by the total uncertainties in the theoretical Raman signal amplitudes of about 3% for the relative R-values and

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5.2% for the ratios. However, further comparisons are needed, including the tritiated species HT, DT and T_2 in a similar gas mixing device (HYDE) as used here. Unfortunately, a unit able to handle these radioactive gases in this way is not yet available.

4. Conclusion

The KATRIN experiment aims to measure the neutrino mass with a sensitivity of $m_\nu = 200\,\mathrm{meV/c}^2$ (90% C.L.). This can only be achieved if systematic uncertainties are minimized. Of utmost importance is the isotopic composition of the tritium gas injected into the source cryostat which is measured inline by Raman spectroscopy. KATRIN requires a trueness of better than 10%, which can be obtained by proper calibration. In this work we have discussed two independent calibration methods, which on their own have individual difficulties. The sampling technique promises high accuracy, but cannot be easily applied to tritiated species. The approach via theoretical Raman signals (theoretical intensities & spectral sensitivity) could cover all isotopologues, but the confidence in the theory is unknown since no experimental literature values exist. In the context of the spectral sensitivity calibration it is worth noting that the use of a solid fluorescence standard, such as the SRM2242 sample used in our measurements, may be judged as being generally advantageous exhibiting low calibration uncertainties, longevity and almost perfect imitation of the Raman scattering region. A comparison in the range of the non-radioactive isotopologues (H_2, HD, D_2) shows agreement of better than 2% for the relative response function obtained by both methods. This is within the estimated uncertainty of the theoretical Raman signal approach of about 3%. Thus, this approach applied for the KATRIN relevant species (T_2, DT, D_2 and HT) will exceed the trueness requirements. Finally, together with a HYDE-type gas mixing facility it should be also possible to extend our methodology to accurately measure relative cross-sections to other gases (especially those which are only stable in mixtures).

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Acknowledgments

References

[1] The KATRIN collaboration, J. Angrik, et al., KATRIN Design Report 2004, FZKA Scientific Report 7090, 2005.

[2] M. Babutzka, M. Bahr, J. Bonn, B. Bornschein, A. Dieter, G. Drexlin, K. Eitel, S. Fischer, F. Glück, S. Grohmann, M. Hötzel, T. M. James, W. Käfer, M. Leber, B. Monreal, F. Priester, M. Röllig, M. Schlösser, U. Schmitt, F. Sharipov, M. Steidl, M. Sturm, H. H. Telle, N. Titov, New J. Phys. 14 (2012) 103046.

[3] S. Fischer, M. Sturm, M. Schlösser, B. Bornschein, G. Drexlin, F. Priester, R. J. Lewis, H. H. Telle, Fusion Sci. Techn. 60 (2011) 925–930.

[4] N. Doss, J. Tennyson, A. Saenz, S. Jonsell, Phys. Rev. C 73 (2006) 025502.

[5] Working Group 2 of the Joint Committee for Guides in Metrology, International vocabulary of metrology - Basic and general concepts and associated

terms (VIM), 3rd edition, JCGM 200:2008, Bureau International des Poids et Mesures (BIPM), 2008.

[6] M. Schlösser, S. Fischer, M. Hötzel, W. Käfer, Proc. Int. School of Physics 'E. Fermi', Course CLXXXII 'Neutrino Physics and Astrophysics', ed. G. Bellini (IOS, Amsterdam; SIF, Bologna), arXiv/1203.4099 (2012) 333–336.

[7] M. Nishi, T. Yamanishi, T. Hayashi, Fusion Eng. Des. 81 (2006) 745 – 751.

[8] R. Lässer, ITER Design Description Document, Tritium Plant and Detritiation Systems, WBS32H, Analytical system, Technical Report, 2001.

[9] M. Sturm, M. Schlösser, R. J. Lewis, B. Bornschein, G. Drexlin, H. H. Telle, Laser Phys. 20 (2009) 493–507.

[10] D. Demange, C. Alecu, N. Bekris, O. Borisevich, B. Bornschein, S. Fischer, N. Gramlich, Z. Köllő, T. Le, R. Michling, F. Priester, M. Röllig, M. Schlösser, S. Stämmler, M. Sturm, R. Wagner, S. Welte, Fusion Eng. Des. 87 (2012) 1206 – 1213.

[11] ISO 6142:2001, Gas analysis - preparation of calibration gas mixtures - gravimetric methods, The International Standard Organisation, Geneva, Switzerland, 2001.

[12] P. C. Souers, Hydrogen Properties for Fusion Energy, University of California Press, Berkeley, CA, USA, 1986.

[13] C. Schwartz, R. J. LeRoy, J. Mol. Spectrosc. 121 (1987) 420–439.

[14] T. Ohta, S. Bouchigny, J.-P. Didelez, M. Fujiwara, K. Fukuda, H. Kohri, T. Kunimatsu, C. Morisaki, S. Ono, G. Rouillé, M. Tanaka, K. Ueda, M. Uraki, M. Utsuro, S. Y. Wang, M. Yosoi, Nucl. Instrum. Meth. A 664 (2012) 347–352.

[15] R. L. McCreery, Photometric Standards for Raman Spectroscopy, in J. M. Chalmers, P.R. Griffith (Eds.), Handbook of Vibrational Spectroscopy, John Wiley & Sons Ltd, Chichester, UK, 2006.

[16] D. Long, The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules, John Wiley & Sons Ltd, Chichester, UK, 2002.

[17] D. K. Veirs, G. M. Rosenblatt, J. Mol. Spectrosc. 121 (1987) 401–419.

[18] R. J. LeRoy, Calculation of the Raman transition matrix elements of all hydrogen isotopologues for 532nm laser excitation, Private communication, 2011.

[19] C. D. Allemand, Appl. Spectrosc. 24 (1970) 348–353.

[20] M. Schlösser, T. M. James, S. Fischer, R. J. Lewis, B. Bornschein, H. H. Telle, J. Raman Spectrosc. (accepted f. pub.), DOI: 10.1002/jrs.4201 (2012).

[21] S. J. Choquette, E. S. Etz, W. S. Hurst, D. H. Blackburn, S. D. Leigh, Appl. Spectrosc. 61 (2007) 117–129.

Accurate Calibration of the Laser Raman System for the Karlsruhe Tritium Neutrino Experiment

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Highlights

▶ Mixing technique using catalytic-reactor to obtain calibrated H_2 : HD : D_2 ratios

▶ Raman sensitivity calibration using NIST-traceable SRM2242 luminescence standard

▶ Combined spectral sensitivity and theoretical intensities for absolute Raman signals

▶ Cross-calibration of H_2, HD and D_2 Raman response functions to better than 2%

Graphical abstract