

SI-Traceable Line Intensity of H₂O near 1.393 μm^{*})

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We recently reported the quantity values of line intensity for H₂O near 1.393 μm in a manner traceable to the International System of Units (SI). This paper briefly describes how to determine the reliable values of the line intensity, mainly focusing on the SI-traceability.

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1. Introduction

Spectroscopy is a powerful and effective tool commonly used in various fields, including chemical analysis, plasma diagnostics, industrial emissions monitoring, atmospheric research, and so on. In particular, spectroscopic methods that can measure the absolute value of an absorption coefficient, such as cavity ring-down spectroscopy (CRDS) [1–3], are of great importance because they can determine the number density of a target gas molecule without reference to measurement standards.

In order to determine the number density of a target gas molecule based on the Beer-Lambert law using high resolution absorption spectroscopy, the quantity value of line intensity for an absorption line, S , is essential. This means that the reliability of the number density measured with such methods is dependent on the reliability of the S value used in the analysis. In order to obtain a reliable S value, the experiment for measuring it should be performed in a manner traceable to the International System of Units (SI).

We recently reported the SI-traceable S values of H₂O near 1.393 μm [4], where the relative expanded uncertainty for strong absorption lines was below 1.8%, which satisfied a measurement uncertainty of 2% to 3% required from climate meteorology for the characterization of Earth's climate [4, 5]. In this paper, we briefly describe how we determined the reliable S values, mainly focusing on the SI-traceability.

The novel feature of this study is the explicit description of a method to establish the SI-traceability of the S value, which has been rarely reported in previous studies despite its metrological importance. Additionally, the study provides theoretical justification for using the S

value to determine itself, addressing the so-called chicken-and-egg issue (see Sec. 3).

The method reported in this study is highly general and, therefore, applicable to other infrared-active molecules and different wavelength regions.

2. Quantities Requiring SI-Traceability

The line intensity of an absorption line is a function of thermodynamic temperature T and related to the strength S_0 at a reference temperature T_0 by [6],

$$S(T) = S_0 \left(\frac{T_0}{T} \right)^{1.5} \exp \left[-\frac{hcE_0}{k_B} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (1)$$

where h is the Planck constant, c is the speed of light, E_0 is the energy of the lower level of the transition, and k_B is the Boltzmann constant. In Ref. [4], a primary standard gas of trace moisture in N₂ gas was measured using a CRDS-based system. $S(T)$ is given by,

$$S(T) = k_B T / (x_w P) \int \alpha(\tilde{\nu}) d\tilde{\nu}, \quad (2)$$

where x_w is the amount fraction of H₂O in the sample cell for the CRDS experiment, P is the pressure inside the cell, α is the absorption coefficient, and $\tilde{\nu}$ is the wavenumber. The integral was performed for an analyzed absorption line. x_w consists of two components, given by,

$$x_w = x_{\text{std}} + x_s, \quad (3)$$

where x_{std} is the amount fraction of H₂O in the primary standard gas and x_s is the stray moisture in the cell, which is unwantedly introduced into the cell and difficult to be removed completely. The primary standard gas was generated using the multi-gas trace-moisture generator (Multi-TMG) [7, 8]. Figure 1 shows a schematic of the gas lines

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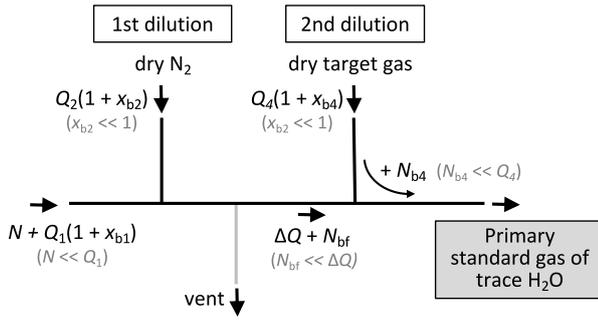


Fig. 1 Schematic of gas lines of Multi-TMG.

in the generator. x_{std} is given by [8],

$$x_{\text{std}} = \frac{\Delta Q \times N}{(Q_1 + Q_2)(\Delta Q + Q_4)} + \frac{\Delta Q(N_{\text{bf}} + x_{\text{b1}}Q_1 + x_{\text{b2}}Q_2)}{(Q_1 + Q_2)(\Delta Q + Q_4)} + \frac{N_{\text{b4}} + x_{\text{b4}}Q_4}{\Delta Q + Q_4}, \quad (4)$$

where Q_1 , Q_2 , Q_4 and ΔQ are the flow rates, N is the evaporation rate of water, N_{bf} and N_{b4} are the desorption rates of moistures in the generator, and x_{b1} , x_{b2} , and x_{b4} are the residual moistures in dry gases (see Ref. [8] for details). In CRDS, α is given by,

$$\alpha(\tilde{\nu}) = \frac{1}{c} \left[\frac{1}{\tau(\tilde{\nu})} - \frac{1}{\tau_0(\tilde{\nu})} \right], \quad (5)$$

where τ and τ_0 are the ring-down times with water and for the baseline of the spectrum, respectively.

Equations (1) - (5) indicate that the quantity values that should be traceable to the SI are T , E_0 , P , $\tilde{\nu}$, τ , τ_0 , x_s , N , Q_1 , Q_2 , Q_4 , ΔQ , N_{bf} , N_{b4} , x_{b1} , x_{b2} , and x_{b4} . The quantity values of h , k_B , and c should be cited from the SI defining constants ($6.62607015 \times 10^{-34}$ Js, 1.380649×10^{-23} J/K, and 299792458 m/s, respectively) [9].

3. Establishment of SI-Traceability

In order to establish the SI-traceability for the S value, the instruments used to measure the quantity values specified in the previous section should be calibrated in a manner traceable to the SI. It should be noted that calibration is an operation that establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated uncertainties, as defined in 2.39 of International Vocabulary of Metrology (VIM) [10]. Therefore, the evaluation of uncertainties other than those documented in the calibration certificates of the instruments is also necessary.

The instruments used to measure T , P , $\tilde{\nu}$, τ , τ_0 , Q_1 , Q_2 , Q_4 , and ΔQ were calibrated in manners traceable to the SI, and the associated uncertainties were also evaluated. The details of these calibrations can be found elsewhere

[4, 7, 8]. The SI-traceability for the remaining quantities, namely E_0 , x_s , N_{bf} , N_{b4} , x_{b1} , x_{b2} , and x_{b4} , is discussed below.

The quantity value and the associated uncertainty of E_0 can be found in the literature [11], which are $136.76165 \text{ cm}^{-1}$ and 0.00001 cm^{-1} , respectively. These values were obtained from the analysis of H_2O spectra of the (010) - (000) band recorded using a high-resolution Fourier-transform spectrometer (FTS). The spectra were calibrated using the wavenumbers of H_2O line positions reported by Guelachvili [12]. These line positions were calibrated using the CO 1-0 and 2-1 bands [13], and the calibration of wavenumber was performed using the atomic Krypton line that was used to define the length in the past. In Refs. [11–13], measurement uncertainties of wavenumbers were evaluated. Thus, the quantity value of E_0 used to determine S was considered to be SI-traceable.

The quantity values of x_s , N_{bf} , N_{b4} , x_{b1} , x_{b2} , and x_{b4} were measured using two CRDS-based instruments; x_s was measured with a CRDS system developed at NMIJ [14] that was also used in Ref. [4], and N_{bf} , N_{b4} , x_{b1} , x_{b2} , and x_{b4} were measured using a commercially available trace-moisture analyzer. Spectra were recorded and analyzed to determine those quantity values for both instruments, without using the indication of the commercially available trace-moisture analyzer. The calculation of the quantity values using spectral data requires an S value, which should be SI-traceable. However, we did not have that value yet, as determining it was the final goal of the study (a chicken-and-egg issue). To address this issue, the following procedures were adopted. x_{std} is rewritten as,

$$x_{\text{std}} = x_{\text{std1}} + x_{\text{std2}} + x_{\text{std3}}, \quad (6)$$

where x_{std1} to x_{std3} correspond to the first to third terms on the right-hand side of Eq. (4). Equation (3) is also rewritten as,

$$x_w = x_{\text{std1}} + x_{\text{std2}} + x_{\text{std3}} + x_s. \quad (7)$$

Here, we assume that Eq. (7) is approximated by,

$$x_w \approx x_{\text{std1}}. \quad (8)$$

It should be noted that the quantity value of x_{std1} could be determined in a manner traceable to the SI by measuring N , Q_1 , Q_2 , Q_4 , and ΔQ . Using Eqs. (2) and (8), we could approximately determine the S value. This value was then used to determine x_{std2} , x_{std3} , and x_s , which were 0 nmol/mol (negligible) [7], 0.60 nmol/mol [7], and 1.25 nmol/mol [4], respectively. The quantity value of x_{std1} in the experiment was 504.32 nmol/mol . The ratio $(0 + 0.60 + 1.25)/504.32 = 0.37 \%$ was sufficiently small in this study, suggesting that the assumption adopted above was appropriate. The influence of this ratio on the S value is discussed quantitatively in the next section. Using these quantity values and Eqs. (2) and (7), the SI-traceable S values with associated uncertainties were obtained. The SI-

Table 1 value and uncertainty.

$\tilde{\nu}/\text{cm}^{-1}$	$S_0 \times 10^{20}/\text{cm}$	Relative expanded uncertainty of S_0 ($k=2$)
7181.15511	1.515	1.72 %
7182.94911	0.3785	1.74 %
7182.20873	0.1602	1.75 %

traceable S_0 values at $T_0 = 296$ K for three strong absorption lines near $1.393 \mu\text{m}$ are given in Table 1 [4], where the relative expanded uncertainty with a coverage factor of $k = 2$ corresponds a 95 % level of confidence for a normal distribution.

4. Discussion

The assumption adopted in the previous section should be reasonable because $x_{\text{std}2}$, $x_{\text{std}3}$, and x_s were unwanted contributions to the experiment, and therefore we developed our measurement system so as to minimize these values as much as possible.

The error in S generated by the approximation with Eq. (8) can be estimated as follows. Equation (2) can be rewritten as,

$$S = aA/x_w, \quad (9)$$

where $a = k_B T/P$ and is a constant factor when T and P are constant, and A is the integrated area given by $\int \alpha(\tilde{\nu})d\tilde{\nu}$. Similarly, the line intensity obtained with the approximation described in the previous section, S_{ap} , is given by,

$$S_{\text{ap}} = aA/x_{\text{std}1}. \quad (10)$$

When the dry gas is introduced into the cell and measured using the CRDS system, where the amount fraction of water of the residual moisture is $x_{\text{std}2} + x_{\text{std}3} + x_s \equiv x_{\text{re}}$, the integrated area should become Ax_{re}/x_w . The mole fraction of water calculated using this integrated area and S_{ap} is given by,

$$x_{\text{calc}} = \frac{aAx_{\text{re}}}{S_{\text{ap}}x_w} = \frac{x_{\text{std}1}x_{\text{re}}}{x_w}, \quad (11)$$

where Eq. (10) is used in the last equality. This value is smaller than x_{re} by a factor of $x_{\text{std}1}/x_w (\approx 1)$. When x_{re} is evaluated in this manner, using Eq. (11) and $x_{\text{std}1} = x_w - x_{\text{re}}$, the amount fraction of water in the standard gas introduced into the cell with the residual moisture with this evaluation is given by,

$$\begin{aligned} x'_w &= x_{\text{std}1} + x_{\text{calc}} = x_w - x_{\text{re}} + \frac{(x_w - x_{\text{re}})x_{\text{re}}}{x_w} \\ &= x_w \left[1 - \left(\frac{x_{\text{re}}}{x_w} \right)^2 \right] = x_w \left[1 - \left(\frac{x_{\text{calc}}}{x_{\text{std}1}} \right)^2 \right]. \end{aligned} \quad (12)$$

The line intensity calculated with x'_w is given by,

$$S' = aA/x'_w. \quad (13)$$

Using Eqs. (9), (12), and (13), we obtained

$$S/S' = x'_w/x_w = \left[1 - \left(\frac{x_{\text{calc}}}{x_{\text{std}1}} \right)^2 \right]. \quad (14)$$

Hence, the contribution of the error caused by the approximation can be evaluated by $(x_{\text{calc}}/x_{\text{std}1})^2 = (0.37\%)^2 = 0.014\%$. This is negligible compared to the relative expanded uncertainty of S_0 (see Table 1). Generally speaking, the effort involved in establishing metrological traceability for each quantity value should be commensurate with its relative contribution to S , as described in NOTE4 of 2.41 in Ref. [10].

5. Conclusion

We explicitly described a method to establish SI-traceability, reinforcing the reliability of our reported S values from a metrological perspective. The influence of desorbed, residual, and stray moisture on the determination of the S value was 0.014 % relative, which was negligible. The method reported in this study is highly general and, therefore, applicable to other infrared-active molecules and different wavelength regions, contributing to the acquisition of more reliable S values.

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