Spectroscopic measurement of the vapour pressure of ice


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We present a laser absorption technique to measure the saturation vapour pressure of hexagonal ice. This method is referenced to the triple-point state of water and uses frequency-stabilized cavity ring-down spectroscopy to probe four rotation–vibration transitions of H$_2$O at wavenumbers near 7180 cm$^{-1}$. Laser measurements are made at the output of a temperature-regulated standard humidity generator, which contains ice. The dynamic range of the technique is extended by measuring the relative intensities of three weak/strong transition pairs at fixed ice temperature and humidity concentration. Our results agree with a widely used thermodynamically derived ice vapour pressure correlation over the temperature range 0°C to −70°C to within 0.35 per cent.

Keywords: water vapour; ice vapour pressure; cavity ring-down spectroscopy

1. Introduction

The saturation vapour pressure of any pure substance is defined as the pressure at which the gas and condensed phases are in thermodynamic equilibrium. It is typically a strong function of temperature, and in the case of ice, varies by more than five orders of magnitude over the range 0°C to −100°C. Accurate knowledge of the temperature dependence of the vapour pressure of hexagonal ice, $e_w(T)$, is the basis for primary standards of humidity generation that use ice-containing saturators to promote mass transfer of water vapour into a carrier gas stream. This thermodynamic quantity is also relevant to many other scientific and technical fields. In atmospheric physics, ice crystals act as condensation nuclei, which promote cloud formation, and thus indirectly affect the albedo of the Earth. In polar regions, stratospheric ice crystals support heterogeneous chemical reactions that are critical to the depletion of ozone. These and other examples, too numerous to mention here, motivate an accurate description of $e_w$ and its variation with temperature.

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The saturation vapour pressure of water at the triple-point temperature, $T_{tp} = 273.16$ K, is well known from the high-accuracy manometric measurements of Guildner et al. (relative uncertainty $< 1.6 \times 10^{-5}$ at the 99% confidence level) [1,2]. In principle, the Clapeyron equation can be integrated from $T_{tp}$ to yield theoretical values of $e_w(T)$ in terms of the heat of fusion of ice and $e_w(T_{tp})$. Notwithstanding relatively small variations in implementation, numerous studies (see Murphy & Koop [3] and references therein) have used this theoretical approach to calculate the vapour pressure of ice by using the triple-point state as a starting point. Since all of these correlations are effectively pinned to the triple-point value, deviations between these correlations tend to grow as the temperature decreases. For temperatures approximately less than $-50^\circ$C, relative differences between predicted values sometimes can approach or exceed 1 per cent. With regard to direct measurements of vapour pressure, the results are subject to far more uncertainty. Unfortunately, there is no measurement set of sufficient high quality that can convincingly provide experimental validation of calculated $e_w(T)$ over a wide range in temperature. Indeed, commonly used measurements reported to date [4] exhibit scatter in the vicinity of $-100^\circ$C, which is about an order of magnitude larger than the expected uncertainty in the theoretical correlations. Thus, we assert that measurements of ice vapour pressure are unable to confirm the relatively low reported uncertainties in their calculated values, especially at temperatures well below that of the triple point of water. Motivated by this state of affairs, our goal is to measure $e_w(T)$ and thus independently bound uncertainty in its calculated value.

In this article, we describe a new experimental method for measuring $e_w(T)$. We use laser absorption spectroscopy to probe four H$_2^{16}$O transitions whose intensities span the range 500 : 1. Measurements are made on steady flow mixtures of water vapour and N$_2$. These samples are prepared with the National Institute of Standards and Technology (NIST) low frost-point generator (LFPG), which is a temperature-regulated humidity standard containing isothermal samples of ice. The intensity of the weakest of these four absorption transitions is determined in terms of the vapour pressure of ice near the triple-point condition. We extend the dynamic range of the technique by measuring the relative intensities of the three remaining weak/strong transition pairs at successively lower ice temperatures and humidity concentrations. This approach yields the temperature-dependent variation in the vapour pressure of ice relative to that at the triple-point condition. Currently, our measurements of $e_w(T)$ extend down to $-70^\circ$C.

We describe how the spectroscopic technique can span a sufficiently wide range in water vapour concentration without seriously compromising measurement precision or accuracy. To demonstrate the integrity of this approach, we present a preliminary analysis of the measurements, and we compare these results to literature values for $e_w(T)$. Our long-term goal is to use this approach to extend the measurement of $e_w(T)$ to $-100^\circ$C, which is the lower temperature limit of our primary standard humidity generator.

2. Spectroscopic measurement of water vapour concentration

The near-infrared absorption spectrum of water vapour is characterized by a large number of discrete lines, each specified by a wavenumber, $\tilde{\nu}_0$ (position), and
temperature-dependent intensity, \( S(T) \), with each corresponding to a transition between molecular rotation–vibration states. A complete description also includes the line-shape function, \( g(\tilde{\nu} - \tilde{\nu}_0) \), which quantifies line-broadening effects. The absorption coefficient, \( \alpha \), corresponds to the fractional loss per unit length of a light beam propagating through a medium with absorber number density, \( n \), and for absorption dominated by a single transition, it is

\[
\alpha(\tilde{\nu}) = nS(T)g(\tilde{\nu} - \tilde{\nu}_0).
\]

In the absence of optical saturation effects and mixing between transitions, the integral of the line-shape function over all wavenumbers is unity. It follows from equation (2.1) that the area of the spectrum, \( A = \int \alpha(\tilde{\nu}) d\tilde{\nu} \), is independent of the actual line shape (which can vary with pressure and temperature) and equal to the product, \( nS \). This key property of linear absorption spectroscopy makes it possible to measure absorber number density over a wide range of pressure and temperature, provided the spectrum area is properly measured and the line intensity and its temperature dependence are known. Conversely, when the absorber number density is known, the transition line intensity can be determined from measurement of the spectrum area. We note further that the more general case of multiple, blended transitions, can be simply modelled as a superposition of isolated transitions of the form given by equation (2.1). As an example, in figure 1, we show the portion of the air-broadened absorption spectrum of water vapour relevant to the present experiment. This calculated spectrum is based on \( T = 296 \text{K} \), a total pressure of \( p = 13.3 \text{kPa (100Torr)} \), a molar fraction of water vapour, \( x = 10^{-3} \) and the line parameters given in the High-resolution transmission molecular absorption (HITRAN) 2008 database [5].
Table 1. List of measured H$_2^{16}$O transitions with transition wavenumbers $\tilde{\nu}_0$, intensities $S$ at $T_r = 296$ K, lower state energies $E''$ and $\beta = d \ln S / d T$. Data are taken from HITRAN [5].

<table>
<thead>
<tr>
<th>line no.</th>
<th>$\tilde{\nu}_0$ (cm$^{-1}$)</th>
<th>$S(T_r)$ cm$^{-1}$/molecule cm$^{-2}$</th>
<th>$E''$ (cm$^{-1}$)</th>
<th>$\beta$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7175.4924</td>
<td>2.905 x 10$^{-23}$</td>
<td>1360.2354</td>
<td>0.0173</td>
</tr>
<tr>
<td>2</td>
<td>7178.4458</td>
<td>1.493 x 10$^{-22}$</td>
<td>602.7735</td>
<td>0.00480</td>
</tr>
<tr>
<td>3</td>
<td>7182.2091</td>
<td>1.541 x 10$^{-21}$</td>
<td>42.3717</td>
<td>-0.00436</td>
</tr>
<tr>
<td>4</td>
<td>7181.1558</td>
<td>1.505 x 10$^{-20}$</td>
<td>136.7617</td>
<td>-0.00281</td>
</tr>
</tbody>
</table>

The temperature dependence of all measured line intensities can be taken into account by assigning the typical reference temperature of $T_r = 296$ K and using

$$
S(T_r) = Q(T_r) \exp \left[ \left( -\frac{h c E''}{k_B} \right) \left( \frac{1}{T_r} - \frac{1}{T} \right) \right],
$$

where $S(T_r)$ is the line intensity at the reference temperature, $h$ is Planck’s constant, $c$ is the speed of light, $k_B$ is the Boltzmann constant, $h c E''$ is the lower state energy and $Q$ is the total internal partition function of H$_2^{16}$O. For small excursions, $\delta T = T - T_r$, the fractional change in the intensity per unit temperature, $\beta = d \ln S / d T$, depends on $E''$ and is nearly linear in temperature such that $S(T_r)/S(T) = 1 / (1 + \beta \delta T)$.

In practice, there is always a finite range over which $\alpha$ can be measured for a particular transition and experimental arrangement. With large values of $nS$, absorption losses become so large that the measurement technique loses sensitivity to absorber concentration. In the opposite limit where sample absorption is weak, the small signal-to-noise ratio of $\alpha$ precludes accurate measurements of $nS$. For this experiment, we extended the measurement range of water vapour concentration by probing the four transitions given in table 1 (labelled 1–4 and indicated in figure 1) whose components have progressively stronger intensities.

We produced steady flow samples of humidified N$_2$ carrier gas with the thermodynamically based LFPG humidity generator described below. The central feature of this system is an ice-coated saturator maintained at temperature $T_s$ and pressure $p_s$. The standard model for a humidity generator of this type gives

$$
x = \left[ \frac{c_w(T_s)}{p_s} \right] f(T_s, p_s),
$$

for the molar fraction of water vapour in which $f(T_s, p_s)$ is the enhancement factor for the gas mixture. For temperatures other than that of the water triple point, we treated $c_w(T_s)$ in equation (2.3) as an unknown quantity. Thus, we used the humidity generator to vary the temperature and hence vapour pressure of an ice sample. This is in contrast to the typical application of the humidity generator in which $c_w(T_s)$ is treated as a known quantity and measurements of $T_s$ and $p_s$ provide $x$. Spectroscopic measurements of the water vapour concentration downstream of the humidity generator were made at pressure $p$.
Table 2. List of tie points (excluding first row) used to measure line intensity ratios. The saturator temperature is given by $t_s = T_s - 273.15\,\text{K}$. Index $i$ corresponds to the transitions labelled in table 1, and $p_i$ and $\alpha_i$ are the cell pressure and peak absorption coefficient, respectively. The first row gives the conditions at which the intensity of line 1 was measured. The vapour pressure at this condition is within 0.16 per cent of the value at the triple point of water.

$$
t_s \quad x \quad p \quad \alpha \quad p_{i-1} \quad \alpha_{i-1}
\begin{array}{cccccc}
(\degree\text{C}) & (10^{-6}) & i & \text{kPa} & (10^{-6}\text{cm}^{-1}) & \text{kPa} & (10^{-6}\text{cm}^{-1}) \\
-0.009 & 5919 & 1 & 2.71 & 4.3 & & \\
-34.8 & 222 & 2 & 13.2 & 2.2 & 1 & 13.2 & 0.47 \\
-49.6 & 40 & 3 & 13.2 & 3.7 & 2 & 13.3 & 0.40 \\
-68.2 & 3.3 & 4 & 12.7 & 3.1 & 3 & 13.2 & 0.30 \\
\end{array}
$$

and temperature $T$. Assuming ideal gas conditions and no net sources or sinks of water vapour in the connecting tubing, the water vapour concentration in the spectrometer was

$$
n = \frac{xp}{(k_B T)}.
$$

(2.4)

The intensity of transition 1, denoted by $S_1$, was measured in terms of the ice vapour pressure at a temperature near the triple point of water, $e_w(T_{tp})$. In order to extend the dynamic range of the technique, it was necessary to use the additional transitions given in table 1. Therefore, the intensities of the other three transitions had to be found independently of $e_w(T_{tp})$ by reference to $S_1(T_r)$. To this end, we measured the respective ratios of areas, $A$, for line pairs at specific values of $x$ that correspond to fixed saturator conditions $T_s$ and $p_s$. We call these values of $x$ 'tie points', and we define the intensity ratio of the line pair $i+1$, $i$ to be $r_{i+1,i} = S_{i+1}(T_r)/S_i(T_r)$. Assuming small temperature excursions, $\delta T = T - T_r$, the intensity ratio is

$$
r_{i+1,i} = \frac{A_{i+1}}{A_i} \frac{T_{i+1}}{T_i} \frac{p_i}{p_{i+1}} \frac{1 + \beta_i \delta T_i}{1 + \beta_{i+1} \delta T_{i+1}}. 
$$

(2.5)

Note that this ratio depends only on the measured spectral areas and temperature and pressure in the absorption spectrometer, but does not depend on $x$ or $e_w(T)$. Furthermore, by successive application of equation (2.5), it follows that $S_2 = r_{21}S_1$, $S_3 = r_{32}r_{21}S_1$ and $S_4 = r_{43}r_{32}r_{21}S_1$. The reference condition for the determination of $S_1$ and the conditions for the three tie points are given in table 2.

With the set of four line intensities $S_1$, $S_2$, $S_3$ and $S_4$ determined as given above, the measured ice vapour pressure, $e_w,m$ is given by

$$
e_{w,m}(T_s) = \frac{k_B T}{f(T_s, p_s) S(T_r)} \frac{p_s}{p} \frac{1}{1 + \beta(T - T_r)}. 
$$

(2.6)

Here, we omit the subscripts indicating the specific transition being probed. We emphasize that equation (2.6) can be recast without any explicit reference to line intensity in terms of ratios of measured spectrum areas, enhancement factors at the saturator conditions, and sample temperatures and pressures. In order to evaluate equation (2.6), we calculated the temperature- and pressure-dependent enhancement factor for the H$_2$O–N$_2$ system. These calculations of
were based on a recent model of the H₂O–N₂ interaction potential given by Tulegenov et al. [6]. All measurements reported here correspond to \(p_s \sim 101\) kPa, and at this pressure, \(f(T_s, p_s) - 1\) ranges from \(4.6 \times 10^{-3}\) to \(8.9 \times 10^{-3}\) over the temperature range \(T_s = 0°C\) to \(-70°C\) for H₂O in N₂. The standard uncertainty in \(f(T_s, p_s)\) increases nearly linearly with decreasing temperature, and varies from approximately \(0.03\) to \(0.06\) per cent over this range of temperature. These calculated values of \(f(T_s, p_s)\) are approximately \(0.1–0.2\%\) greater than those reported by Hyland & Wexler [7] for the H₂O–air system. We conclude that the measured ice vapour pressure is relatively insensitive to uncertainty in \(f(T_s, p_s)\). Nevertheless, investigation of this correction in further detail could be carried out by making measurements at lower saturator pressure, since \(f(T_s, p_s) - 1\) is nearly proportional to \(p_s\).

We also point out that Guildner’s low-uncertainty value for the triple point of water vapour pressure [1,2] \((e_w = 611.657\) Pa\) corresponds to water substance with a natural isotopic abundance of H, D \((Z = 1, M = 1, 2)\), and \(^{16}\)O, \(^{17}\)O and \(^{18}\)O \((Z = 8, M = 16, 17, 18)\). On a molar fraction basis, the natural atomic abundance for H is \(0.99984426(5)\) and those of \(^{16}\)O, \(^{17}\)O and \(^{18}\)O are \(0.9976206(5), 0.0003790(9)\) and \(0.0020004(5)\), respectively [8]. Based on a random mixture of these atoms, the three most abundant isotopologues and respective molar fractions of water are H\(_2\)\(^{16}\)O \((0.997493)\), H\(_2\)\(^{18}\)O \((2.00014 \times 10^{-3})\) and H\(_2\)\(^{17}\)O \((3.7895 \times 10^{-4})\). In the present analysis, we assumed that all samples were at natural isotopic abundance and no significant isotopic fractionation occurred with changes in ice temperature. As a test of this assumption, measurements of the spectrum area of a H\(_2\)\(^{18}\)O transition \((\tilde{\nu} = 7184.45637\) cm\(^{-1}\)) were also carried out over a range of saturator temperatures \((0°C\) to \(-60°C)\). We found that the relative temperature dependence of the H\(_2\)\(^{18}\)O spectrum area was nearly identical to those of the H\(_2\)\(^{16}\)O transitions given in table 1, supporting the assertion that fractionation effects were not significant. Thus, under this assumption of negligible isotopic fractionation, the H\(_2\)\(^{16}\)O probed in this study was an accurate proxy for the vapour pressure of ice at natural isotopic abundance.

3. Experiment and results

All measurements were carried out at the NIST in Gaithersburg, MD, USA. As we have described previously [9], this work involved two complementary, high-precision experimental systems: (i) the LFPG humidity standard generator and (ii) an NIST-built frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) absorption spectrometer. The LFPG serves as the primary method of humidity generation at NIST for trace quantities of water vapour [10,11]. Its ice-containing saturator can be controlled over the range \(0°C\) to \(-101°C\), with a combined standard uncertainty of approximately \(6\) mK [12]. The FS-CRDS system has been previously described [9,13], and is based on the cavity ring-down spectroscopy (CRDS) technique. Its principal components include an actively length-stabilized ring-down cavity and a continuous-wave distributed feedback diode laser emitting in the wavenumber range 7175–7185 cm\(^{-1}\). In order to reduce the adverse effects of background water vapour adsorption and desorption, the internal surface area of the ring-down cavity was reduced nearly tenfold over the previous system by eliminating a pair of welded bellows. Apart from this
Modification, all components of the FS-CRDS system were identical to those described by Hodges and co-workers [9,13]. Measurements were made at two flow rate conditions: 0.7 standard l min\(^{-1}\) and 0.22 standard l min\(^{-1}\), respectively. The lower flow rate was used to minimize the pressure drop in the cell, which occurs when the cell is maintained at a low pressure. Measurements and fluid mechanics models of the gas flow revealed that the pressure drop between the cell and the downstream pressure gauge scaled with \(p^{-1}\), with a constant of proportionality depending on the total flow rate. To quantify this effect on the FS-CRDS measurements, spectrum areas were obtained at fixed total flow rate, fixed water vapour molar fraction and over a range of cell pressures. The largest pressure correction (which corresponded to the low flow rate at a cell pressure of 2.67 kPa) was just 0.34 per cent. The required pressure correction was only 0.07 per cent for the data obtained at the high flow rate and cell pressure of 13.3 kPa.

The choice of line profile used in equation (2.1) is critical to the analysis of measured spectra. Although the Voigt profile (VP) is commonly used to model water vapour spectra at these conditions, we opted for a more sophisticated line-shape analysis in order to avoid systematic biases in the fitted peak areas. Specifically, we used the Galatry profile (GP) as well as the speed-dependent Nelkin–Ghatak profile (SDNGP) to model the line-shape function \(g(\tilde{v} - \tilde{v}_0)\). In our previous study, we compared these and other line-shape functions used in the analysis of the water transitions probed here [9]. Briefly, the GP and SDNGP are based on a soft-collision model and hard-collision model, respectively, and in addition to pressure broadening, the GP accounts for the effects of Dicke narrowing, whereas the SDNGP models Dicke narrowing and speed-dependent broadening and shifting. With the peak area \(A\) as a fitted parameter, profiles were fit to the measured FS-CRDS absorption spectra with a Levenberg–Marquardt nonlinear least-squares algorithm. Except for the case of transition 2, there was some line blending, as evidenced by the contribution of weak residual lines to the observed spectra. For these spectra, all observed lines were modelled to optimize the fit quality and minimize systematic bias in the determination of \(A\) associated with the dominant transition. Our spectrum model also included a linear baseline to take into account the empty cavity losses, Rayleigh scattering and continuum absorption from the wings of distant lines. Along with the LFPG and FS-CRDS systems, the present line-shape analysis was a key component of our measurement technique, which enabled us to precisely measure \(S_1(T_r)\) and the intensity ratios, \(r_{21}, r_{32}\) and \(r_{43}\). This approach should be contrasted to commonly implemented CRDS methods used in the humidity community, which are based on measurement of the peak absorption and the assumption of a VP with known Lorentzian width [14].

In figure 2, we present a measured spectrum and least-squares fit to transition 2, for the case corresponding to the first tie-point condition given in table 2. The quantity on the ordinate of figure 2, labelled \((cr)^{-1}\), represents the baseline plus absorption losses of the ring-down cavity, where \(\tau\) is the measured ring-down decay constant at each frequency detuning \(c(\tilde{v} - \tilde{v}_0)\). This figure illustrates our measurement precision and the sensitivity to choice of line profile. Fits of the GP and the SDNGP yield the smallest r.m.s. residuals, with the SDNGP giving the highest signal-to-noise ratio (peak absorption/residual r.m.s.) equal to 4000 : 1. The residuals to the VP fit have a large non-random component, and reveal that this profile does not capture the physical line shape, and near
Figure 2. (a) Measured spectrum (circles) and least-squares fit of the SDNGP (solid line) for transition 2 at $x = 2.22 \times 10^{-4}$, $p = 13.3$ kPa. The data represent an average of 10 spectra. (b) The residuals for fits of the VP, GP and SDNGP to the measured spectrum. Note the factor of 10 scale change for the VP case compared with the GP and SDNGP cases. (Online version in colour.)

line centre, the VP fit residuals are about 20 times larger than those of the SDNGP. Typical of our other measurements, the GP and SDNGP yielded areas that differed by less than 0.1 per cent, whereas the VP fit yielded an area 1.27 per cent less than that of the SDNGP. In the final analysis, we used the SDNGP to fit all measured spectra, and we typically used the line parameters previously measured by Lisak et al. [9] in our laboratory. Since these line-shape parameters were obtained over a range of gas pressure encompassing the conditions of the present study, the SDNGP fits are expected to provide an accurate measure of the spectrum areas. We note that except for transition 2, which was isolated from spectral interferences, analysis of the measured spectra for the other three water vapour transitions given in table 1 included the effects of neighbouring lines, all of which could be assigned using the HITRAN database. In the case of transition 1, there was a total of 10 interfering transitions considered, comprising six, one, and two lines of $\text{H}_2^{16}\text{O}$, $\text{H}_2^{18}\text{O}$, $\text{H}_2^{17}\text{O}$ and $\text{D}_2\text{O}$, respectively. For transition 3, there were five interfering $\text{H}_2^{16}\text{O}$ lines, and for transition 4, there was one other $\text{H}_2^{16}\text{O}$ line considered in the spectrum curve fitting.

The foregoing analysis yielded $e_{w,m}(T)$ at the three tie points given in table 2 plus an additional value based on measurements of transition 1 at the saturator temperature $t_s = -19.770^\circ\text{C}$. In figure 3, we show the fractional difference between $e_{w,m}(T)$ and the commonly used $e_w(T)$ correlations given by Wexler [15]
Figure 3. Temperature dependence of the fractional difference between our measured vapour pressure, \( e_{w,m} \), and the literature values, \( e_{w,lit} \), reported by Wexler [15] (circles) and Marti & Mauersberger [4] (triangles). The solid lines are based on curve fitting the physically based expression \( e_w = e_w(T_{tp})(T/T_{tp})^{c_1} \exp[c_2(1/T - 1/T_{tp}) + c_3(T - T_{tp})] \) [3] to our data, where \( c_1 \), \( c_2 \) and \( c_3 \) are fitted parameters. The abscissa corresponds to \( t = T - 273.15 \text{K} \). (Online version in colour.)

Table 3. Measured saturation vapour pressure of water vapour as a function of temperature. \( u_r(e_{w,m}) \) is the relative standard uncertainty in \( e_{w,m} \) and \( \Delta_W \) and \( \Delta_M \) are the present results relative to the correlations of Wexler [15] and Marti & Mauersberger [4], respectively.

<table>
<thead>
<tr>
<th>( t ) (°C)</th>
<th>( e_{w,m} ) (Pa)</th>
<th>( u_r(e_{w,m}) ) (%)</th>
<th>( \Delta_W ) (%)</th>
<th>( \Delta_M ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−19.770</td>
<td>105.47</td>
<td>0.39</td>
<td>−0.065</td>
<td>−0.449</td>
</tr>
<tr>
<td>−34.775</td>
<td>22.886</td>
<td>0.41</td>
<td>−0.013</td>
<td>−0.881</td>
</tr>
<tr>
<td>−49.629</td>
<td>4.1338</td>
<td>0.42</td>
<td>0.340</td>
<td>−1.045</td>
</tr>
<tr>
<td>−68.226</td>
<td>0.33936</td>
<td>0.44</td>
<td>−0.087</td>
<td>−2.018</td>
</tr>
</tbody>
</table>

and Marti & Mauersberger [4], and in table 3, we present our measured values for \( e_{w,m}(T) \) and the combined relative standard uncertainties \( u_r(e_{w,m}) \). These uncertainties are approximately 0.40 per cent and increase only slightly as one steps through the set of three tie points. The combined uncertainty in \( e_w(T) \) is dominated by some irreproducibility in the fitted spectrum area of transition 1 (approx. 0.35%), which is measured near the water triple-point temperature. In the order of diminishing importance, other contributing uncertainties include sample pressure (approx. 0.1%), spectrum area temperature correction (approx. 0.06%), LFPG saturator pressure (approx. 0.05%) and enhancement factor (approx. 0.03%). Since the \( e_w(T) \) expression given by Wexler [15] was based on the International Practical Temperature Scale of 1968 (IPTS-68), before evaluating this correlation, we converted our measured saturator temperature

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from the International Temperature Scale of 1990 (ITS-90) to IPTS-68 using the conversion given in Preston-Thomas & Quinn [16]. Our measured values of the ice vapour pressure are in excellent agreement with the correlation of Wexler [15], with an r.m.s. relative difference of 0.09 per cent. Importantly, these preliminary measurements are precise enough to resolve differences between the correlations of Wexler [15] and the widely cited correlation of Marti & Mauersberger [4] for temperatures as high as $-20^\circ C$.

4. Conclusions

We have presented a new method for measuring the vapour pressure of ice. Our approach exploits the precision, linearity and sensitivity of the FS-CRDS method, first-principles models of absorption line shapes for spectrum analysis, and the thermal stability, and low temperature and pressure uncertainty of the ice-containing LFPG standard humidity generator. Note that our experimental results for the ice vapour pressure span a water vapour concentration range of approximately 1800:1 and are effectively pinned to the triple-point vapour pressure given by Guildner et al. [1,2]. Moreover, because the measurements are based upon ratios of spectrum areas, the results do not depend upon prior knowledge of the intensities of the absorption lines under investigation. Our measurements yielded combined uncertainties in ice vapour pressure at the sub-per cent level over a wide range of temperature and concentration. Extension of this technique to temperatures as low as $-100^\circ C$ should provide an even more rigorous test of experimental and theoretical correlations for the vapour pressure of ice.

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