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Infrared Band Strengths and Optical Constants of D_2O Ices, with New Measurements on H_2O Ices and a Band-Strength Estimate for HDO

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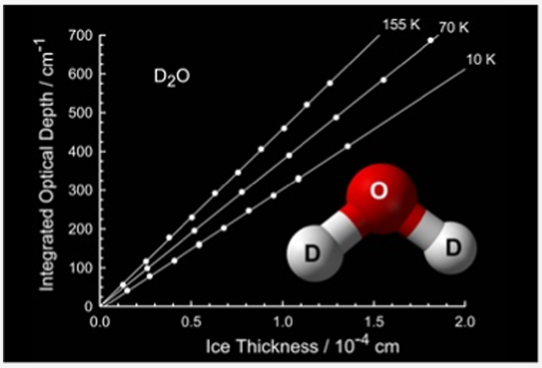
ABSTRACT: The infrared band strengths of D_2O and H_2O ices have been calculated from new spectra at 10, 70, and 155 K. In contrast to nearly all previous work, integration ranges are provided and close attention has been paid to the use of multiple ice samples and Beer's Law (Beer−Lambert) plots to support the claim of a linear trend of band intensity with ice thickness. Optical constants have been calculated as averages from the results of multiple measurements, in what again seems to be the first such approach for water ices. A 200% discrepancy in H_2O optical constants in the literature is addressed and a resolution suggested. The new infrared intensity results for D_2O-ice are the first in many years and are compared to previous work from almost a half-century ago. The same new results are used to estimate the intensity of the O−D stretching mode of HDO in ices at 10 K, without the need for warming to higher temperatures. The new estimate can be used for calculating HDO abundances from ice observations made with the James Webb Space Telescope.



KEYWORDS: *IR spectroscopy, band strengths, astrochemistry, amorphous solids, ices*

1. INTRODUCTION

Studies of deuterium-containing molecules, deuteration, and deuterium fractionation have a long history among astronomers and astrochemists. Early observational work began with the detections and identifications of isotopologues such as HD, DCN, and HDO in the gas phase of the interstellar medium (ISM).[1−3] Theoretical models have since expanded our understanding of deuterium chemistry in the solid phase, such as on interstellar grains.[4−7] However, laboratory investigations of deuterium chemistry in icy solids of the ISM remain somewhat less developed than observational, theoretical, and experimental gas-phase studies to the extent that few deuterated species have been identified and quantified in interstellar ice analogs. In this paper we address this situation by considering deuterium variants of solid water, the most common interstellar ice.

Over the past 15 years, our research group has investigated infrared (IR) intensities of over 50 compounds as icy solids, each being a compound of interest to astrochemists. We have covered most of the common classes of organics and many inorganics, but relatively little attention has been paid to isotopic variants and solid water. In this paper we consider deuterated water, D_2O, one of the simpler and presumably more-common fully deuterated compounds in interstellar and Solar System ices. Interstellar D_2O has been reported,[8] while cometary D_2O was detected during the Rosetta mission,[9] each detection being of the gas-phase molecule.

Our goal with frozen D_2O here is not so much to raise the chances of this compound being detected in an extraterrestrial environment with present-day technology, but to provide data to aid laboratory investigations of extraterrestrial chemistry. The need for accurate IR intensities of D_2O is amply demonstrated by an examination of the literature. Recent work by Khan et al.[10] with D_2O-ice on ice crystallization cited an older study for IR intensity results,[11] and although that paper cited an even older work, no band strengths are found there.[12] A study of atom implantation in ices by Zheng et al.[13] employed D_2O to discriminate against atmospheric and other sources of contamination, but again little earlier work was available for determining ice thicknesses. Similar concerns relate to investigations of D_2O by Öberg et al.,[14] an

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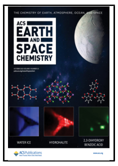

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investigation of isotopic exchange in cometary ices,[15] and our own studies of D/H exchange.[16]

Here we report new IR spectra of amorphous and crystalline D_2O ices along with IR band strengths and optical constants. We also describe some of our recent measurements of IR intensities of amorphous and crystalline H_2O-ice, with an emphasis on comparisons to earlier work and addressing a contradiction between two of the more recently published measurements. An estimate of the band strength for the O−D stretching vibration of HDO in amorphous H_2O-ice is also made. However, before presenting our new results on water ices, we first describe some of the older frequently cited papers on D_2O-ice, commenting on each from a 21st-century perspective.

2. PREVIOUS WORK—BAND STRENGTHS

The most influential early publications on IR spectra of D_2O ices probably are those of Giguère and Harvey,[17] Hornig et al.,[18] and Ikawa and Maeda,[19] and we begin with comments on each.

The paper of Giguère and Harvey[17] seems to have been the first to present and compare the mid-IR spectra of H_2O-ice and D_2O-ice. That publication documented IR peak positions, but its lack of both ice thicknesses and a scale on the vertical axes of spectra prohibits calculations of IR intensities. A nonlinear vertical scale was provided in a subsequent paper from Hornig et al.,[18] but again with no ice thicknesses given. Positions of H_2O, HDO, and D_2O were reported, but no intensities.

The first report of IR intensities of solid water ices was apparently that of Ikawa and Maeda[19] who studied solid H_2O and solid D_2O, reporting IR spectra and band strengths at 113 K. "No significant differences" were said to apply between intensities of amorphous and crystalline ices, but no details were given. Areas were said to be determined "as usual" for the strongest IR band (O−H and O−D stretches) of the ices, again with no details. No integration ranges were supplied, no spectral resolution was stated, and the densities used to convert band areas into IR intensities were not given. Band strengths were reported for the two strongest features of solid water, the stretching and libration bands. Intensity results for HDO also were reported, as were Beer's law plots based on up to five ices. These depended on knowing abundances of HDO in each ice sample, but again few details were given. Ice thicknesses were not stated for the IR spectra in the figures and the same refractive index was used both for amorphous and crystalline ices. The thicknesses in that same paper were measured at 173 K where ices were made, but IR spectra were only integrated after the ices were cooled to 113 K. Concentrations were expressed as percents, presumably molar (molecular) and not mass or volume percents, but this was not stated. However, despite all of these omissions and concerns nearly or perhaps entirely all quantitative IR studies of deuterated water ices within the astrochemical community can be connected to or cite the work of Ikawa and Maeda.[19]

3. PREVIOUS WORK—OPTICAL CONSTANTS

A more recent comparison of IR intensities of H_2O-ice and D_2O-ice is found in the paper by Bergren et al.[12] who calculated optical constants $n(\tilde{\nu})$ and $k(\tilde{\nu})$ of water ices as opposed to IR band strengths. Sample preparation, IR measurements, and optical-constants calculations were clearly described. The difficulty of comparing to earlier work was explicitly noted, as was the uncertainty in measuring thicknesses of D_2O ices by interferometry due to uncertainties in refractive index. Results were presented only for the intense O−H and O−D stretching features of H_2O-ice and D_2O-ice, respectively, those being the bands most clearly separated from others.

The procedure of Bergren et al.[12] for calculating optical constants has been followed by others,[20] including our own group,[21] and like the work of Ikawa and Maeda the results of Bergren et al. have been widely used. Nevertheless, after almost a half century it is easy to recognize uncertainties in that same paper. For example, it is not stated that more than one ice of each type was examined, it is not clear if Beer's Law plots (i.e., different ice thicknesses) were prepared to check that the band strengths reported varied linearly with ice thicknesses, the optical constants reported are for a lower spectral resolution than now used in most laboratories, results at 10 K relevant to interstellar chemistry were not included, details of the authors' method of measuring ice thickness were not described, and the software used for $n(\tilde{\nu})$ and $k(\tilde{\nu})$ calculations was not published.

4. NEW INFRARED INTENSITIES

The previous work on IR intensities for D_2O-ice is from 1978 and earlier and was done with dispersive spectrometers before Fourier-transform instruments and their inherent advantages became standard in the field. Just as important is that the earlier D_2O-ice studies do not appear to have been checked, verified, and so on for nearly 50 years. Therefore, in the present paper we use Fourier-transform technology to reexamine the IR intensities of solid D_2O at three temperatures with a higher-resolution and a lower temperature than previously employed and with explicit attention to integration limits, ice densities, and refractive indices. Both band strengths and optical constants are reported, with the latter being made available in digital form.

As this is our group's first extensive examination of IR intensities of water ices it seemed desirable to extend our measurements from D_2O to H_2O and to compare the results to the band strengths and optical constants already published. However, we found it surprisingly difficult to locate Beer's Law plots for amorphous H_2O-ice at 10 K, perhaps the temperature and ice form most often used in laboratory studies of interstellar ice analogs. As for optical constants, several sets have been published since the early work of Bergren et al.,[12] but the two most recent sets have $k(\tilde{\nu})$ values that differ by about 200%. New measurements on H_2O-ice seemed called for and are presented here. Finally, the IR band strength of the O−D stretching vibration in the half-deuterated HDO molecule is also of interest, but cannot be measured in the same way as for H_2O and D_2O ices. Some of the literature on HDO in ices will be reviewed in the Discussion section and a new band strength estimate given. Our greatest interest is in the O−D and O−H stretching regions of our IR spectra as they appear to be the most astrochemically relevant.

An important part of our new work is the use of multiple ices with multiple thickness to derive IR intensities. Many papers on IR intensities of water ices and other compounds assume, or appear to assume, the applicability of Beer's Law, but do not support that assumption with measurements on multiple ices of different thicknesses. It is difficult to know how much confidence to place in any work reporting spectral intensities based on what amounts to single-point calibration curves. Therefore, for both D_2O and H_2O ices, our band strengths and optical constants are derived from multiple ices and multiple thicknesses. Comparisons are made to some of the earlier studies in our Discussion section.

5. LABORATORY PROCEDURES

The methods followed and the equipment used were the same as employed in our recent studies of IR band strengths and optical constants.[22−24] Readers familiar with the methods used to obtain and measure IR spectra of ices at cryogenic temperatures might wish to skip to the next section.

The D_2O (99.96% D) used in this work was purchased from MilliporeSigma and was used as received aside from routine degassing with freeze−pump−thaw cycles and liquid nitrogen. Our H_2O was HPLC grade obtained from Fisher Chemical and it too was used as received aside from routine degassing.

Ices were prepared by condensation of room-temperature D_2O or H_2O vapor onto a precooled CsI substrate in a vacuum chamber (10^{-8}−10^{-9} Torr), the substrate temperature being 10, 70, or 155 K. Each of the resulting ices grew at a rate that increased its thickness by about 1 μm h^{-1} as determined by laser interferometry with $\lambda = 670$ nm. Interference fringes were recorded and their number (N_{fr}) was used to calculate an ice's thickness (h) with eq 1, where n_{670} was the index of refraction of the ice at 670 nm and $\theta = 3.57 \pm 0.04°$ was the angle between the incident laser beam and a line drawn perpendicular to the substrate.

$$h = \frac{N_{fr}\lambda}{2\sqrt{{n_{670}}^2 - \sin^2\theta}} \tag{1}$$

See also our recent papers[22−24] or the book by Heavens.[25]

The IR spectra of ices made as just described were recorded in a standard transmission mode at a resolution of 1 cm^{-1} and 100 to 200 scans per spectrum. The spectral range was from 5000 to 400 cm^{-1}, although the signal was somewhat noisy below about 450 cm^{-1}. Absorbance spectra of ices of various thicknesses were measured and each IR band of interest was integrated. Graphing the left-hand side of eq 2 below as a function of thickness h gave a Beer's Law plot (Beer−Lambert plot) with a slope $\rho_N A'$ that when divided by number density ρ_N yielded the band strength A', here in units of cm molecule^{-1}, for the IR feature of interest.

$$\ln(10)\int_{\text{band}}(\text{Absorbance})\mathrm{d}\tilde{\nu} = (\rho_N A')h \tag{2}$$

This is essentially the original method of Hollenberg and Dows[26] aside from the use of a laser to generate the interference fringes.[27] A similar procedure and similar equipment have been used in about 40 of our papers published since 2014.

Band strengths of D_2O and H_2O are reported here for the stretching and libration features, but optical constants were calculated and are presented for a wider IR range. Beer's law plots were prepared for amorphous ices at 10 and 70 K and crystalline ones at 155 K. Correlation coefficients were 0.995 and higher. Ice densities and refractive indices for eqs 1 and 2 were measured at lower pressures (~10^{-10} Torr), just as before.[28] For the determination of n, see the paper of Tempelmeyer and Mills.[29] Ice densities were measured with a quartz-crystal microbalance as before.[28]

Optical constants $n(\tilde{\nu})$ and $k(\tilde{\nu})$ were calculated with the iterative Kramers−Kronig method described earlier.[21] The software used is free and open source. See https://science.gsfc.nasa.gov/691/cosmicice/or https://zenodo.org/records/4429276.

In line with our earlier papers, we refer to graphs of integrated optical depth as a function of ice thickness as simply Beer's Law plots, although we recognize that other names are related to the historical development of such relations.[30]

6. RESULTS

The values of n and ρ used in the present study are listed in Table 1. Each quantity was measured for H_2O-ice condensed at the temperature listed from room-temperature H_2O vapor. The use of H_2O values for D_2O is in line with previous work.[12,19] Note that the number densities of solid H_2O and solid D_2O can be taken as the same, but that the mass densities of D_2O are higher than those of H_2O.

Table 1. Refractive Indices and Densities Used for H_2O and D_2O Ices[a]

T/K	n_{670}	$\rho(H_2O)$/g cm^{-3}	ρ_N/molecules cm^{-3}
10	1.234 ± 0.008	0.719 ± 0.005[b]	2.403 × 10^{22}
70	1.294 ± 0.001	0.840 ± 0.001[b]	2.807 × 10^{22}
155	1.329 ± 0.008	0.931 ± 0.004[b]	3.111 × 10^{22}

[a] The wavelength used for measuring refractive indices (n) was 670 nm. Each n_{670} and $\rho(H_2O)$ value in the table is the average of three determinations (three ices). Values used at 10 K were measured at 19 K and values used at 155 K were measured at 150 K. Values used at 70 K were measured at 70 K. [b] Although the mass densities (ρ) of H_2O and D_2O differ, the number densities (ρ_N) were taken as the same for the present work.

6.1. D_2O Ices. Figure 1 shows IR spectra of D_2O ices grown at 10, 70, and 155 K, with their spectra recorded at those same temperatures and with each ice having a thickness of about 0.5 μm. The ices at 10 and 70 K were amorphous, but the one at 155 K was crystalline. From spectra of D_2O ices at different thicknesses at each temperature, Beer's law plots were constructed and from their slopes band strengths were obtained. Figure 2 shows data for the O−D stretching (~2500 cm^{-1}) and libration bands (~600 cm^{-1}) of solid D_2O at 10, 70, and 155 K. The resulting band strengths for this feature are listed in the upper half of Table 2.

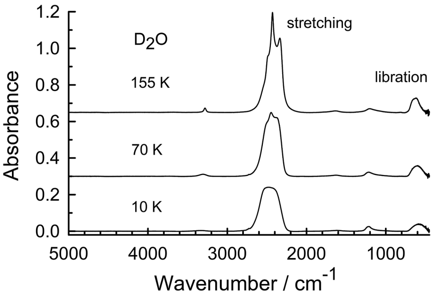

Figure 1. Mid-IR spectra of D_2O ices made, and spectra recorded, at the temperatures indicated. Each ice's thickness was about 0.50 μm. Spectra are offset vertically for clarity.

Optical constants were calculated from spectra of D_2O ices at 10, 70, and 155 K. For each temperature, at least seven spectra (seven ice thicknesses) were used and then the resulting $n(\tilde{\nu})$ and $k(\tilde{\nu})$ were averaged for that temperature. See Figures 3−5 for the results. We have not found

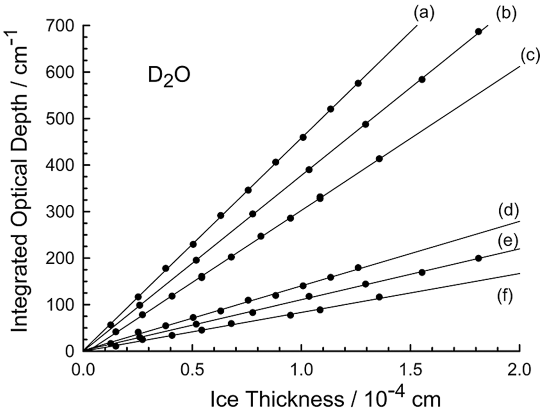

Figure 2. Integrated optical depths of the two strongest D_2O bands at three temperatures. Lines (a), (b), and (c) are for the stretching region (~2480 cm^{-1}) for ices at 155, 70, and 10 K, respectively. Lines (d), (e), and (f) are for the libration band (~570 cm^{-1}) for ices at 155, 70, and 10 K, respectively. Note that optical depths for (d), (e), and (f) have been multiplied by 3 for clarity.

Table 2. Infrared Band Strengths ($A'/10^{-18}$ cm molecule^{-1}) of D_2O and H_2O Ices[a]

ice	T/K	stretching region	libration band
D_2O	10	129 (2482 cm^{-1})	11.6 (572 cm^{-1})
D_2O	70	134 (2447 cm^{-1})	13.0 (598 cm^{-1})
D_2O	155	147 (2430 cm^{-1})	14.9 (620 cm^{-1})
H_2O	10	234 (3297 cm^{-1})	32.2 (757 cm^{-1})
H_2O	70	256 (3260 cm^{-1})	32.3 (796 cm^{-1})
H_2O	155	274 (3228 cm^{-1})	31.7 (827 cm^{-1})

[a] Band positions are in parentheses and are approximate in most cases due to a band's great breadth, the exceptions being the stretching regions at 70 and 155 K. Integration ranges were 2800−2000 and 755−453 cm^{-1} for D_2O and 3800−2800 and 1050−465 cm^{-1} for H_2O.

quantitative IR results for D_2O-ice in the literature corresponding to those in either Table 2 or Figures 2−5.

Note that mid-IR absorption coefficients $\alpha(\tilde{\nu})$ can be calculated found from the optical constants $k(\tilde{\nu})$ in this paper using $\alpha(\tilde{\nu}) = 4\ \pi\ \tilde{\nu}\ k(\tilde{\nu})$. Absorption cross sections $\sigma(\tilde{\nu})$ for D_2O and H_2O can be found from $\sigma(\tilde{\nu}) = \alpha(\tilde{\nu})/\rho_N$ using the number densities ρ_N in Table 1.

6.2. H_2O Ices. Figure 6 shows IR spectra we recorded of four amorphous H_2O ices condensed at, and spectra recorded at, 10 K and having thicknesses, denoted h, of about 0.25, 0.50, 0.75, and 1.00 μm. The areas of the stretching mode near 3300 cm^{-1} and the libration band near 800 cm^{-1} were measured in each spectrum and then converted to integrated optical depth, which is the quantity on the left in eq 2. Plotting the left-hand side of that equation against thickness h produced Beer's Law plots as already described. Figure 7 shows the result for the 10 K amorphous H_2O ices of Figure 6 plus three others. Despite work on the IR intensities of H_2O-ice going back nearly 60 years to Ikawa and Maeda,[19] it is difficult to find Beer's law plots like those in Figure 7. This is particularly surprising for 10-K ices given that laboratory astrochemists probably have studied and used amorphous solid H_2O at or near 10 K more often than any other compound at any other temperature.

The work just described was repeated at 70 and 155 K for amorphous and crystalline H_2O, respectively. The resulting band strengths for all three temperatures are shown in the lower half of Table 3, each value based on at least seven ices (seven thicknesses). Optical constants were calculated for each 10-K spectrum in Figure 6 and then averaged to give the values of $n(\tilde{\nu})$ and $k(\tilde{\nu})$ shown in Figure 8. Values calculated for crystalline H_2O at 155 K will be shown in the Discussion and compared to literature results.

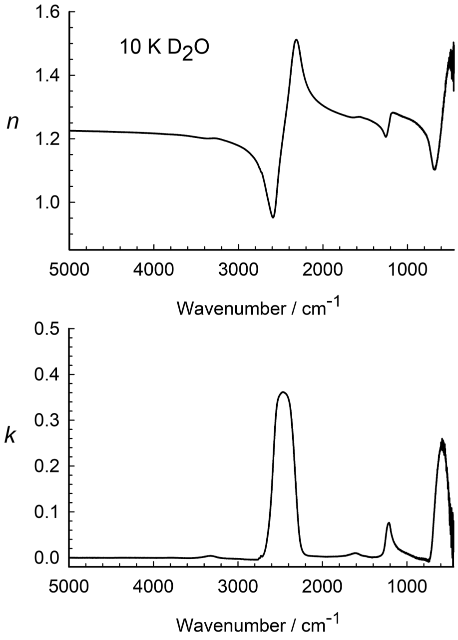

Figure 3. Infrared optical constants for amorphous D_2O-ice at 10 K.

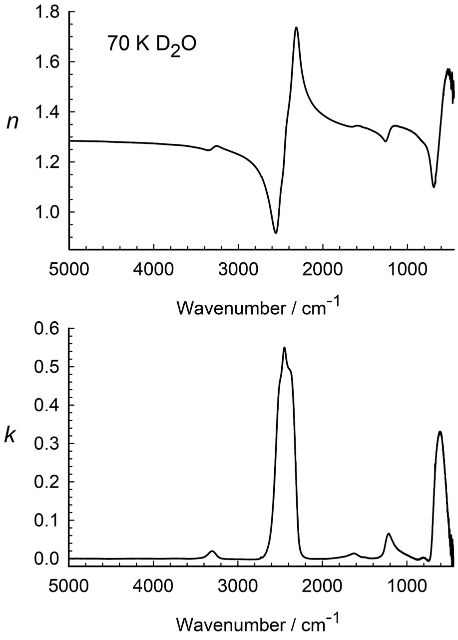

Figure 4. Infrared optical constants for amorphous D_2O-ice at 70 K.

6.3. Uncertainties and Errors. One source of error in calculating IR band strengths and optical constants that has long been recognized is the measurement of ice thickness. Our approach was to use laser interferometry, the "gold standard" for such measurements on icy solids. The method requires an ice's index of refraction, which we measured (Table 1), and involved simply recording interference fringes as an ice was grown. We can easily measure to a twentieth of a fringe,

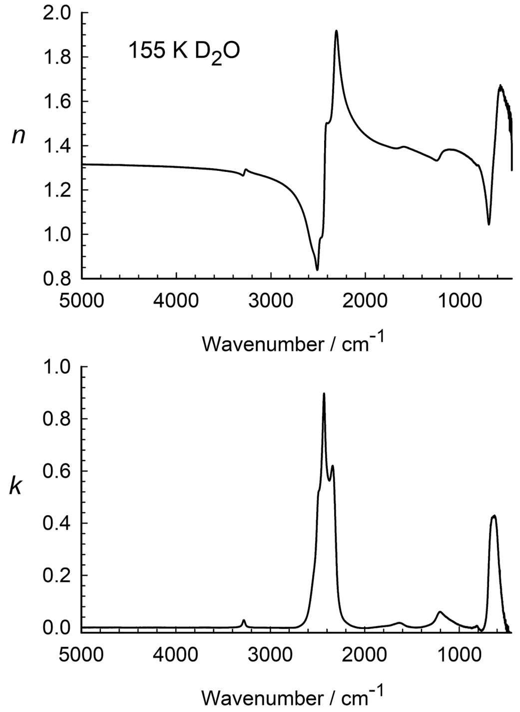

Figure 5. Infrared optical constants for crystalline D_2O-ice at 155 K.

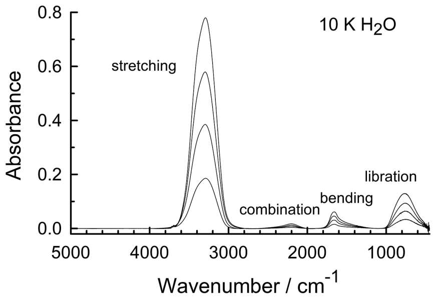

Figure 6. Mid-IR spectra of four amorphous H_2O ices made, and spectra recorded, at 10 K. The ice thicknesses were about 0.25, 0.50, 0.75, and 1.00 μm. Labels show assignments to four IR regions.

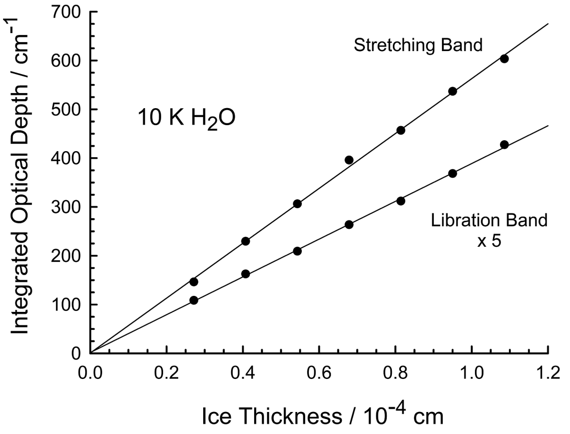

Figure 7. Integrated optical depths of the two strongest bands in the spectra of Figure 6 to which results from three other spectra have been added. Note that the integrated optical depths for the libration band have been multiplied by 5 for clarity.

corresponding to an uncertainty of ±0.01 μm in thickness for our ices given our laser's wavelength of 670 nm = 0.670 μm.

Table 3. Infrared Band Strengths Reported for Amorphous D_2O

source	Ikawa and Maeda[19]	this work
temperature/K	113	10
refractive index n	1.31	1.234
density/g cm^{-3}	not reported	0.719
ice thickness range/μm	~0.2−0.8	0.25−1.1
integration limits stated?	no	yes
Beer's Law plot(s) reported?	yes	yes
Beer's Law plot(s) shown?	yes	yes
A' (stretching band)/cm $molecule^{-1}$	1.20×10^{-16}	1.29×10^{-16}
A' (libration band)/cm $molecule^{-1}$	1.5×10^{-17}	1.16×10^{-17}

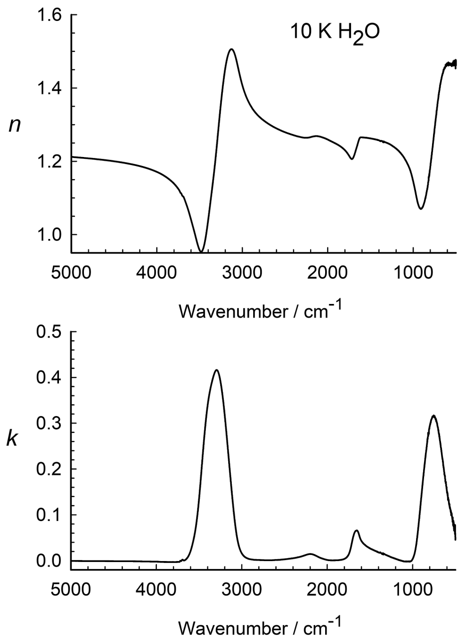

Figure 8. Infrared optical constants for amorphous H_2O-ice at 10 K.

Band areas were measured with the GRAMS/AI software package (version 9.3, Thermo Fisher), with repeated determinations giving a variation of only about 1% in integrated optical depth. A propagation-of-error analysis and least-squares fitting of Beer's Law data, taking into account uncertainties in both ice thickness and integrated optical depth,[31,32] gave an uncertainty in slope and band strength of about 2%. Little influence on A' was found for small changes in refractive index of an ice or the baseline of a spectrum. An ice's density had a greater influence on band strengths, but the density uncertainties in Table 1 are so small that such variations hardly changed the final uncertainty of 2% in band strengths.

Close inspection of the D_2O spectra and optical constants in this paper reveals a small absorbance near 3300 cm^{-1}. That feature is assigned to the O−H stretching vibration of HDO, formed by reaction of D_2O and residual H_2O in our vacuum system. The same contaminant can also be seen in the spectra of Zheng et al.[13] and Khan et al.[10] who worked with ultrahigh-vacuum systems. The extent of such contamination is sometimes hard to judge in earlier papers on D_2O-ice as authors do not always show the relevant spectral region.[12,19] The areas of this band in our IR spectra were 1% or less of the largest D_2O feature at all temperatures and so were neglected.

The published[19] O−H band strength in HDO was used to estimate the mole %HDO in our ices, resulting in answers again on the 1% level. Changes in the D_2O band strengths from those reported here were never larger than in the third significant figure, below any claim of uncertainty.

7. DISCUSSION

7.1. D_2O Ices. Table 3 compares conditions used and band-strength results for amorphous D_2O in our work and that of Ikawa and Maeda.[19] Not knowing either the ice density or the integration ranges used in the latter, and given the large difference in temperatures, it is hard to decide if the reasonable agreement for A' (stretching band) is anything more than serendipitous. Note that the published value of A' for the libration band in Ikawa and Maeda[19] is incorrect. It relies on scaling A' values from a 90%-deuterium ice to a 100%-deuterium level. The published A' value for the stretching band indeed increases, as it should, but the published value of the libration band falls. Whether this is from an arithmetic mistake or a typographical error is not known.

In some ways, literature comparisons are easier for optical constants than for band strengths as calculations of $n(\tilde{\nu})$ and $k(\tilde{\nu})$ do not require either an ice density or integration limits. However, the only D_2O-ice optical constants we have found for comparison to our work are those of Bergren et al.[12] at 77 and 150 K for amorphous and crystalline D_2O, respectively. Each set of $n(\tilde{\nu})$ and $k(\tilde{\nu})$ was restricted to the O−D stretching region around 2440 cm^{-1}. Figures 9 and 10 compare those published results with our own. Given the differences in time and technology between the two sets of measurements, the agreement is quite good. Table 4 summarizes the conditions used and the results for the 77 K measurements. A similar table applies to the optical constants of crystalline D_2O except that the temperature was 150 K in Bergren et al.[12] and 155 K in our work.

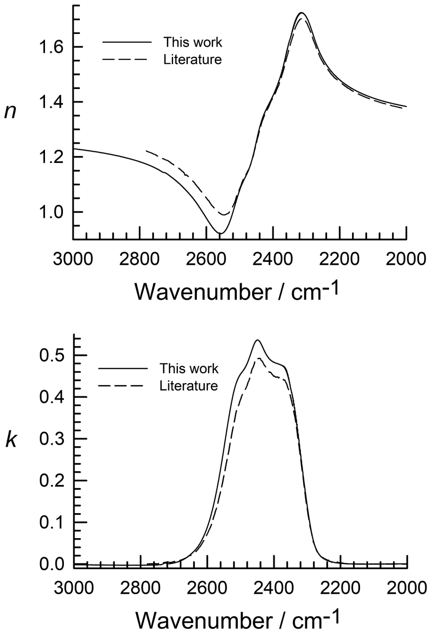

Figure 9. Infrared optical constants for amorphous D_2O-ice at 70 K from this work and from Bergren et al.[12] at 77 K.

7.2. H_2O Ices. Our results with amorphous H_2O-ice at 10 K seem to be the only such published work that is backed by a Beer's Law plot with explicitly stated integration limits and in-house measurements of n and ρ. It is unfortunate that the lack of such relevant details in earlier publications prevents exact comparisons to our work. For example, the early paper of Ikawa and Maeda[19] showed Beer's Law plots for water ices, but did not state the phase, the densities, or the integration limits and they were for a much higher temperature (113 K) than 10 K. The publication of Mastrapa et al.[33] gave integration limits, but there is no indication that more than one ice was examined for each band strength reported and the density used was not clear. Conversely, the paper of Bouilloud et al.[34] relied on Beer's Law graphs (not shown) and gave the ice density adopted, but did not state integration limits when presenting band strengths of amorphous H_2O-ice. Table 5 summarizes these observations.

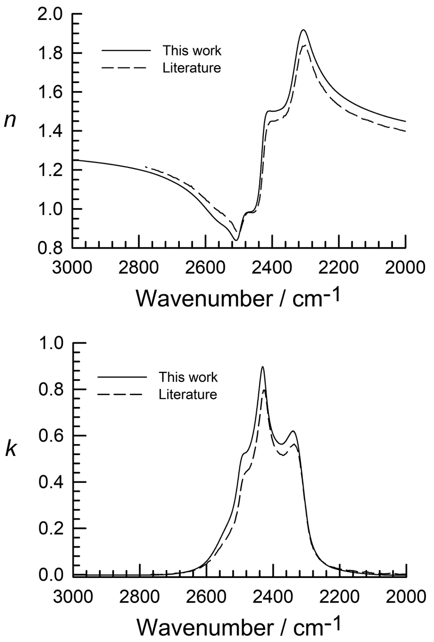

Figure 10. Infrared optical constants for crystalline D_2O-ice at 155 K from this work and from Bergren et al.[12] at 150 K.

Table 4. Optical Constants Reported for Amorphous D_2O

source	Bergren et al.[12]	this work
temperature/K	70	10
refractive index n	1.31[a]	1.234
number of ices used?	not reported	7
used averages of $n(\tilde{\nu})$ & $k(\tilde{\nu})$?	not reported	yes
iterative method used?	yes	yes
IR range(s)/cm^{-1}	~2700−2000	5000−450

[a] The authors pointed out that this n value was likely too large.

In Figure 11 we compare our optical constants for amorphous H_2O to those of Mastrapa et al.[33] and Rocha and Pilling.[35] The disagreement between the latter two is severe. We suspect that the reason is a mistake in Rocha and Pilling[35] in not converting from an absorbance scale to an optical-depth scale, which would explain a factor of about 2 in the $k(\tilde{\nu})$ values. Our results clearly favor the work of Mastrapa et al.[33] The agreement is reasonable from 5000 to 3000 cm^{-1}, but it is increasingly poor at lower wavenumbers. Possible reasons for the discrepancies are differences in how the spectral baseline was chosen and the fact that the literature results are from a computer routine that was not iterative in $n(\tilde{\nu})$ and

Table 5. Infrared Band Strengths Reported for Amorphous H_2O

source	Ikawa and Maeda[19]	Mastrapa et al.[33]	Bouilloud et al.[34]	this work
temperature/K	113	25	25	10
refractive index n	1.31	1.29	1.27	1.234
density/g cm^{-3}	not reported	uncertain	0.87	0.719
ice thickness range/μm	~0.2−0.6	0.26−0.36	not reported	0.25−1.1
integration limits stated?	no	yes	no	yes
Beer's Law plot(s) reported ?	yes	no	yes[a]	yes
Beer's Law plot(s) shown ?	yes	no	no	yes
A' (stretching band)/cm $molecule^{-1}$	2.32×10^{-16}	1.9×10^{-16}	1.5×10^{-16}	2.34×10^{-16}
A' (libration band)/cm $molecule^{-1}$	2.74×10^{-17}	2.5×10^{-17}	not measured	3.22×10^{-17}

[a] Beer's Law plots were not shown, but were said to have been used. However, the regression line on such plots was forced to go through (0,0), which is not a data point.

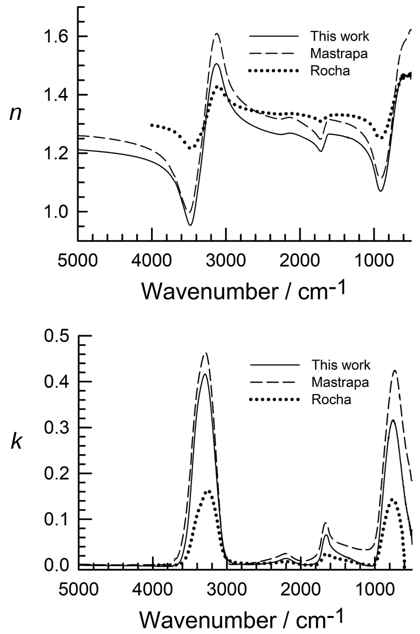

Figure 11. Infrared optical constants for amorphous H_2O-ice at 10 K from this work and from Mastrapa et al.[33] at 15 K and Rocha and Pilling at 12 K.[35]

$k(\tilde{\nu})$. That the software used is not open source prohibits its independent testing. Finally, the temperature used by Mastrapa et al.[33] is about 5 K higher than the 10 K used here, which could lead to a small difference in results. Again, Table 5 compares the conditions and results of our work to those of Mastrapa et al.[33] Table 6 does the same for optical constants of the amorphous ice.

Having results for crystalline H_2O-ice, we also can compare to earlier work, as seen in Table 7. Again there are ambiguities, but the band-strength results of Mastrapa et al.[33] appear to agree with our own. Figure 12 shows that there is excellent agreement between that paper and this one for the optical constants of crystalline H_2O.

Table 6. Infrared Optical Constants Reported for Amorphous H_2O

source	Mastrapa et al.[33]	this work
temperature/K	25	10
refractive index n	1.29	1.234
number of ices used?	unknown	4
used averages of $n(\tilde{\nu})$ & $k(\tilde{\nu})$?	unknown	yes
iterative method used?	no	yes
IR range/cm^{-1}	4000−455	5000−450

Comparisons also are possible to even earlier publications, but they too would suffer from differences and omissions in key factors. All in all, the literature results for amorphous and crystalline H_2O-ice are in reasonable agreement with our own if all of the omissions and variations in previous work are ignored.

7.3. IR Band Strengths of HDO in Ices. The O−D band strength of the half-deuterated HDO molecule is of interest to observational and laboratory astrochemists, but it is impossible to start with liquid HDO and measure the IR band strengths of HDO-ice in the same way that band strengths of H_2O-ice and D_2O-ice were measured here by starting with liquid H_2O and liquid D_2O. The reason is that HDO molecules in any putative liquid HDO sample will undergo reaction (3) below giving a mixture of the three isotopic variants.

$$\mathrm{HDO} + \mathrm{HDO} \rightarrow \mathrm{H_2O} + \mathrm{D_2O} \tag{3}$$

The laboratory challenge is then to separate the O−H contributions of HDO and H_2O in the corresponding intense IR band near 3300 cm^{-1} and then doing the same for the O−D contributions of HDO and D_2O for the IR band near 2440 cm^{-1}.

In contrast to this laboratory obstacle, it is relatively easy to estimate the O−D band strength of HDO in a water-rich ice, which is the solid-phase environment of most interest. In the first two rows of Table 8 we list our A' values for the stretching vibrations of amorphous H_2O and D_2O ices at 10 K. Also listed are band strengths for the stretching vibrations of liquid samples at room temperature.[36] In the far-right column are the liquid-to-solid ratios of A' values. Taking 0.662 as the average ratio, we use that figure as a scaling factor and apply it to the O−D band strength for HDO in liquid water. This gives, for an ice at 10 K, A'(O−D in HDO, 10 K) = A'(O−D in HDO, 295 K)/0.662 = 3.89×10^{-17} cm $molecule^{-1}$/0.662 = 5.88×10^{-17} cm $molecule^{-1}$.

Our estimate for A'(O−D, HOD) is listed in Table 9 along with several published values for comparison, about which concerns can be raised in each case. The earliest report on HDO band strengths is from Ikawa and Maeda.[19] Numerous problems related to that paper have already been described, but the authors' A'(O−D, 113 K, HDO) = 5.0×10^{-17} cm $molecule^{-1}$ has been used or referred to, either directly or indirectly, in many subsequent studies. Ikawa and Maeda began by mixing liquid H_2O and liquid D_2O, with H_2O in large excess to drive the reaction below to the right.

Table 7. Infrared Band Strengths Reported for Crystalline H_2O

source	Ikawa and Maeda[19]	Mastrapa et al.[33]	this work
temperature/K	113[a]	150	155
refractive index n	1.31	1.32[b]	1.329
density/g cm^{-3}	not reported	0.931[b]	0.931
ice thickness range/μm	~0.2–0.6	0.26–0.36	0.25–1.1
integration limits stated?	no	yes	yes
Beer's Law plot(s) reported and shown ?	yes	no	yes
A' (stretching band)/cm molecule^{-1}	2.32×10^{-16}	2.7×10^{-16}[c]	2.74×10^{-16}
A' (libration band)/cm molecule^{-1}	2.74×10^{-17}	3.0×10^{-17}	3.17×10^{-17}

[a] The ice was made and its thickness was measured at 173 K, but it then was cooled to 113 K for IR intensity measurements. [b] Taken from the literature. See Mastrapa et al.[33] for details. [c] It is not clear if this A' includes the entire O–H stretching region as A' values also were given for two shoulders off of the largest band.

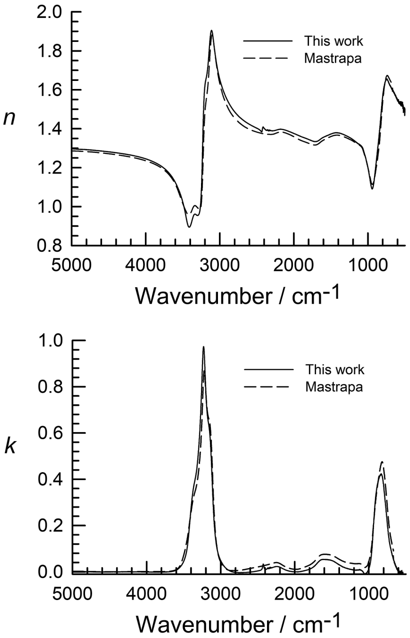

Figure 12. Infrared optical constants for crystalline H_2O-ice at 155 K from this work and from Mastrapa et al. at 150 K.[33]

Table 8. Comparison of IR Band Strengths—Stretching Vibrations[a]

band strength/cm molecule^{-1}	295 K Liquid Bertie et al.[36]	10 K solid this work	ratio
A'(O–H in H_2O)	1.57×10^{-16}	2.34×10^{-16}	0.671
A'(O–D in D_2O)	8.42×10^{-17}	1.29×10^{-16}	0.653
A'(O–D in HDO)	3.89×10^{-17}	(5.88×10^{-17})	0.662

[a] A' value in parentheses is a predicted value. See the text.

$$H_2O + D_2O \rightarrow HDO + HDO \tag{4}$$

The vapor above the resulting liquid mixture was then condensed onto a precooled substrate to make an ice that was mostly H_2O with a smaller amount of HDO present.

It was assumed by Ikawa and Maeda and by other authors using the same method that the HDO abundance in their mixture was unchanged from the initial liquid solution, to the vapor formed, and then to the resulting ice, two phase changes and three different phases. This uncertainty was avoided in a later study by Dartois et al.,[37] who adopted a photochemical approach to estimate the O–D band strength in HDO. However, the method used was not supported by either a demonstration on a system already studied or a reference to one and it assumed an unverified statistical distribution of H and D atoms in photoproducts. The method also assumed a constant ratio among the product yields of H_2O, HDO, and D_2O, but no growth curves were shown for support. Also, a factor of 2 was used in an estimate of a band strength for an O–H vibration, for which no justification was supplied, and no reference was given in support of the O–H band strength used for H_2O-ice. The band strength reported was A'(O–D, 10 K) = 3.6×10^{-17} cm molecule^{-1} for HDO in an ice containing H_2O, CH_4, CO_2, CO, and perhaps other products.[37] A higher value was later adopted by some of the same authors,[38] A'(O–D) = 4.3×10^{-17} cm molecule^{-1}, an average of the values in Ikawa and Maeda[19] and Dartois et al.[37] at 113 and 10 K measured by two different methods. No justification was provided for the new value. Both the original and revised values of A'(O–D, HDO) are given in Table 9.

Instead of either growing an HDO-containing ice at 113 K or generating one photochemically at 10 K, Gálvez et al.[39] prepared HDO in H_2O-ice by condensing at 14 K the vapor over an H_2O + HDO liquid mixture, prepared as in reaction (4), and then warming the ice to 150 K to crystallize it. The area of HDO's O–D stretching band at 150 K, and the assumed initial HDO percent abundance in the initial liquid mixture, were combined with a band strength at 150 K for H_2O-ice taken from Mastrapa et al.[33] to calculate an HDO column density and from there a band strength, A'(O–D, 150 K, HDO) = 6.4×10^{-17} cm molecule^{-1}. The resulting value at 14 K is listed in Table 9. Left unsaid was that Mastrapa et al.[33] specifically mentioned and avoided the derivation of their A' values for crystalline ices prepared by warming from ~10 K, as opposed to an ice being made by condensation at 150 K. Whether the error involved in ignoring that distinction is large, small, or negligible is not described in the paper of Gálvez et al.[39] Neither the earlier papers of Dartois et al.[37] nor that of Gálvez et al.[39] reported measurements at multiple ice thicknesses.

The final line of Table 9 gives A'(O–D, HDO) from a recent paper by Slavicinska et al., who followed a procedure similar to that of Gálvez et al. and used those authors' result at 150 K as a reference value.[40] The resulting A' at 15 K was, not surprisingly, about the same as in Gálvez et al., demonstrating the method's reproducibility.—As an aside, the paper of Slavicinska and twenty-one coauthors uses the phrases "amorphous HDO" and "crystalline HDO" multiple times, but those two solids have never been prepared. Presumably the authors are referring to a comparatively small amount of HDO dispersed in either amorphous or crystalline H_2O.

Table 9. Band Strengths of the O−D Vibration of HDO in Ices

source	A'(O−D, HDO)/cm molecule^{-1}	comments
this work	5.9×10^{-17}	estimate for A' at 10 K based on new IR spectra; n and ρ values given; integration limits supplied; Beer's Law plots (ices with >1 thickness studied)
Ikawa and Maeda (1968)[19]	5.0×10^{-17}	measured at 113 K; no density given for either amorphous or crystalline ices; see text for many comments and concerns
Dartois et al. (2000)[37]	3.6×10^{-17}	photochemical method used, but not verified; not clear how A'(O−D, HDO) at 10 K was extracted; no data reported for more than 1 ice thickness; no integration limits given
Dartois et al. (2000)[38]	4.3×10^{-17}	average of previous two values, but no justification given; no data reported for more than 1 ice thickness; no integration limits given
Gálvez et al. (2011)[39]	4.1×10^{-17}	A' at 14 K after warming ice to 150 K; no data reported for more than 1 ice thickness; no integration limits given; intensity based on literature A'(OH, H_2O, 150 K) value[a]
Slavicinska et al. (2024)[40]	4.2×10^{-17}	A' at 15 K after warming ice to 150 K; no data reported for more than 1 ice thickness; no integration limits given; intensity based on literature A'(OD, H_2O, 150 K) value[b]

[a] Ice thickness calculated from literature result for a single-thickness measurement by Mastrapa et al[33] [b] Ice thickness calculated from literature result for a single-thickness measurement[39] that was based on an earlier literature result for a single-thickness measurement by Mastrapa et al[33]

Other investigators have used other approaches when needing an O−D band strength. Some have simply adopted the original results of Ikawa and Maeda[19] or they have used results related to them. As examples, see Teixeira et al.[41] and Faure et al.[15] See also the work of Urso et al.[42] who chose as reference measurements the O−H band strength originally reported by Hagen et al.[20] and the O−D band strength of Dartois et al.,[38] which in turn depends on Ikawa and Maeda.[19] In analyzing James Webb Space Telescope (JWST) spectra for solid HDO abundances, Slavicinska et al. used work by Gálvez et al.,[39] that in turn depends on earlier studies as already described.

The band strengths in Table 9 can be charitably interpreted as converging on the region from about 4×10^{-17} to 6×10^{-17} cm molecule^{-1} over a range of temperatures. However, a rigorous analysis recognizes that various methods and assumptions have gone into the measurements described, with different omissions of checks and details and with only the work of Ikawa and Maeda deriving band strengths from multiple ice thicknesses. Seen this way, attractions of our A' estimate, as simple as it is, include it being for 10 K, being based on measurements with multiple ice thicknesses, fitting comfortably close to the region of literature values, and relying only on a single scaling factor. Looking forward, it seems that no Beer's Law plot for HDO in H_2O ices has been published in the almost 50 years since the paper of Ikawa and Maeda.[19] A plot for ices near 10 K has never been published and would be welcome.

8. SUMMARY AND CONCLUSIONS

For the first time, IR band strengths and optical constants have been calculated for amorphous and crystalline D_2O-ice with all measurements and calculations being done in the same laboratory. The importance of specifying key quantities such as integration limits, refractive indices, and densities, has been stressed, each being needed for accurate, quantitative lab-to-lab comparisons and for identifying discrepancies between reported results. The necessity of avoiding IR intensity measurements based on a single ice thickness, which amount to a one-point calibration, is emphasized. Not only are these concerns described and illustrated for D_2O-ice, IR band strengths also are reported for H_2O-ice that, for the first time, take all of these factors into account. Band strengths based on Beer's Law plots have been measured and presented for both amorphous and crystalline H_2O-ice for the first time in almost 60 years and for the first time ever at the 10 K important for interstellar chemistry. Since all of the literature IR band strengths for amorphous H_2O-ice at 10 K are accompanied by omissions of detail, we suggest that future observational studies, such as with JWST, use the values in this paper. The same suggestion applies to the optical constants reported here, to which we strongly suggest that only open-source software be used for any future such calculations. Literature band strengths of HDO have been examined and, in light of various concerns, a new estimate of the O−D band strength in HDO has been made.

Comparisons between our new results and the older ones should again be mentioned before closing. In recent years we have examined IR spectra and intensities for solid forms of oxidized and reduced carbon compounds, oxidized and reduced nitrogen compounds, alcohols and thiols, and most recently two acids and an aldehyde.[24] In every case, mistakes were found in the literature, including incorrect identifications and measurement errors of over 100%. Our tables and figures show that the numerical results of our new and the literature measurements for D_2O and H_2O ices agree to within one significant figure and an order of magnitude. The degree to which this level of agreement is fortuitous or not is hard to judge due to the difficulties, omissions, and so on in the literature already mentioned.

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Notes

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