CONF-760524-1

Lawrence Livermore Laboratory

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April 21, 1976

This paper was prepared for submission to the International
Journal of Mass Spectrometry and Ion Physics and presentation
at the Conference on Mass Spectrometry and Allied Topics,
May 9-14, 1976, San Diego, CA.

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HYDROGEN-DEUTERIUM EXCHANGE IN WATER VAPOR: THE MASS
SPECTROMETRIC SENSITIVITIES AND THE EQUILIBRIUM CONSTANT

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ABSTRACT

The equilibrium constant, K_{HDO} , for the reaction $\text{H}_2\text{O} + \text{D}_2\text{O} = 2\text{HDO}$ can be expressed as an intensity ratio, I , measured mass spectrometrically, times a sensitivity ratio, S , measured in mass spectrometric calibration experiments. The latter is difficult to measure and previously was assumed to be unity. The 2.4% discrepancy between K 's from theoretical calculations and direct mass spectrometric measurements might be explained by another value of S . We report an indirect measurement of S using a pulsed-molecular beam quadrupole mass filter that has a unique three-chamber, three-leak gas inlet system. The results show the sensitivities are probably equal and therefore $S = 1$. Systematic errors were found in the procedure, however, which precluded an unambiguous test of the theory.

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INTRODUCTION

The term "sensitivity" is used in two ways in mass spectroscopy. It often means the minimum partial pressure that can be detected by an instrument. It is also a defined quantity relating mass spectrometric intensity to partial pressure of a gaseous species. In the latter sense, the mass spectrometric sensitivity is

$$S_i = \frac{I_i}{P_i}, \quad (1)$$

where S_i is the sensitivity, I_i is the mass spectrometric intensity in arbitrary units, and P_i is the partial pressure of the i th component on the high pressure side of the leak into the instrument vacuum chamber. In principle, the sensitivity can be determined by measurements or calculations of the basic molecular and instrument parameters such as molecular ionization cross section, extraction efficiency of the electron bombardment ion source, transmission efficiency of the mass filter or spectrometer, and gain of the electron multiplier. Because of the difficulty of determining these parameters, one usually measures the sensitivity by a direct calibration experiment. Known pressures of the pure gas are admitted into the inlet system, the intensities recorded, and the sensitivity calculated. Since $P_i = I_i/S_i$, this sensitivity is then used to convert intensities to partial pressures of that gas in a mixture. When pure gases are available for sensitivity calibrations, this procedure works quite well. A different situation exists, however, in the isotope exchange reaction discussed below.

The equilibrium constant, K_{HDO} , for the gas phase reaction,

can be expressed as,

$$K_{\text{HDO}} = \frac{p_{\text{HDO}}^2}{p_{\text{H}_2\text{O}} \cdot p_{\text{D}_2\text{O}}} = \frac{I_{\text{HDO}}^2}{I_{\text{H}_2\text{O}} \cdot I_{\text{D}_2\text{O}}} \cdot \frac{S_{\text{H}_2\text{O}} \cdot S_{\text{D}_2\text{O}}}{S_{\text{HDO}}^2} \quad (3)$$

The term containing the I's is the intensity ratio I, and the term containing the S's designates the sensitivity ratio, S.

The constant, K_{HDO} , has been measured numerous times in the past ten years by direct mass spectrometric measurements [1-5], and in each case was assumed to be equal to the intensity ratio. This implies, of course, that the sensitivity ratio is unity, which could be a result of

$$S_{\text{H}_2\text{O}} = S_{\text{HDO}} = S_{\text{D}_2\text{O}} \text{ or } S_{\text{HDO}} = \sqrt{S_{\text{H}_2\text{O}} \cdot S_{\text{D}_2\text{O}}}.$$

There is a rationale for both propositions. The assumption that $S = 1$, however, has been very useful because of the difficulty in measuring the sensitivity ratio in the system. The problems with this assumption are illustrated below.

The values of the intensity ratios determined by direct mass spectrometric methods are shown in Table 1.

All are in excellent agreement except for the values from Ref. [5]. A difference in the value of S was suggested to explain this discrepancy [5]. Furthermore, the 2% discrepancy between the values of I in Ref. [1-4] and recent theoretical calculations [6-8] of $K_{\text{HDO}} = 3.85$ at 25°C might be the result of a value of S different from unity.

The measurement of the sensitivities of isotopic species of water is complicated by the phenomenon known as memory effect. If a nearly pure H_2O sample is analyzed in a mass spectrometer, followed by a nearly pure D_2O sample, the instrument responds as if a mixture of H_2O , HDO , and D_2O had been added. This is due to the rapid exchange at room temperature of D_2O with H_2O on the surfaces of the inlet system and the high vacuum system of the instrument. This memory effect is overcome by rinsing with the new sample (D_2O) until equilibration with water is accomplished. Another technique to minimize the memory effect in the mass spectrometer vacuum system is pulsed-molecular-beam mass spectroscopy [2]. Further complications arise from the rapid disproportionation of HDO to H_2O and D_2O at room temperature. It is therefore impossible to isolate a nearly pure sample of HDO for calibration in a direct experiment. It is evident that an indirect measurement of S , though difficult and less precise than a direct measurement, might be valuable in rationalizing differences between measured values of I and between theoretical and experimental values.

We devised an indirect method to measure the mass spectrometric sensitivities of H_2O , HDO , and D_2O . The apparatus consisted of three identical (as nearly as possible) gas inlet systems; one each for H_2O , D_2O , and an approximately 50 atom percent D mixture of H_2O , HDO and D_2O ; and a quadrupole mass filter. The memory effect was minimized in the gas inlet system by equilibration and in the mass filter chamber by using a pulsed molecular-beam method [2]. The intensities of H_2O , HDO , and D_2O were determined by alternately adding a sample of the pure gases or the mixture in the appropriate

inlet system at a known pressure, measuring the intensity, pumping out the gas, and then continuously repeating the process. The sensitivity ratio was determined from the experimental data by an iterative method using a small digital computer.

EXPERIMENTAL

Reagents

The D_2O was provided by Bio-Rad Laboratories* and was used without purification. The H_2O was distilled and used without further purification. All water samples were degassed when attached to the vacuum system by alternately freezing, pumping, and thawing in the sample tube.

Apparatus

The apparatus in this study was similar to systems previously used [9] except for the gas inlet system and molecular beam-chopping apparatus. A schematic diagram of the three-gas-inlet systems is given in Fig. 1. Each system was made as equal in volume as possible and had a servo-controlled leak valve with a capacitance manometer to maintain constant pressure in the expansion chamber.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

The unique feature of these systems is shown in Fig. 2. This schematic representation shows the molecular leaks into the quadrupole mass filter as viewed from the ionizer. Notice the three gas expansion chambers that are external to the mass filter vacuum chamber. Each system has a tube leading from the expansion chamber into the mass filter chamber. These tubes meet in a 120° array constructed such that they all interface to each other. The 13×10^{-3} -cm-diameter leaks are drilled through the chamber walls at 120° spaced as close together as possible. As the chopper wheel rotates, it alternately cuts off and lets through the beam from any of the three holes. The chopper wheel has 40 windows evenly spaced around its edge. A photodiode pickup generates the chopper synchronizing signal for the data system. The disk is spun at 375 rpm by a 24-V DC motor. The result is a beam on and off time of 2×10^{-3} s each. Although care was taken to make the systems identical, we expected differences. It is extremely difficult to make such small pin-hole leaks identical. Therefore the three systems must be calibrated against one another.

When we first tried the pulsed-molecular-beam technique on this system, we were dismayed to discover that the chopped fraction of the signal was only about 10% of the total, which would reduce the precision of our measurements. In our original work [2], the chopped portion of the signal was about 40%. We were apparently losing our signal because of poor definition of the molecular beam. We reduced this problem by placing a shroud between the chopper wheel and the ionizer of the mass filter, which channelled the molecular beam into the electron beam. This technique increased the chopped signal to approximately 90% of the total signal (see Fig. 3).

Data System

The output from the electron multiplier of the quadrupole mass filter was fed to a wide-band operational amplifier operating in a charge-to-voltage mode. This signal then went to a voltage-to-frequency converter through a pulse amplifier to a digital synchronous detector. The voltage-to-frequency mode of operation, rather than straight-pulse counting, was required because the output from the synchronous detector is the difference between the chopped and unchopped beams; it was therefore impossible to make a system dead-time correction.

A minicomputer with 8K of core and with magnetic tape units for interactive storage was used as an on-line data acquisition and reduction processor. The synchronous detector was interfaced to the computer as an accumulator-transfer device and the difference between chopped and unchopped beams for each channel was transferred in parallel by computer software command.

The digital synchronous detector is set to add 5 chopped times and 5 unchopped times for a channel time of 0.02 s. The computer provides the sweep for the quadrupole mass filter. This sweep interface controls the sweep rate as well as the channel timing by an operator-set clock. The clock is actually set a little slower than the 0.02 s channel time required by the synchronous detector to allow proper channel synchronization after the data transfer. The sweep is divided into 256 channels: 128 channels for the up-sweep and 128 channels for the down-sweep. This mode of sweeping eliminates long-term signal drifts.

Computer Software

The software for the system is a modified version of FOCAL. The standard FOCAL as supplied by the Digital Equipment Corporation does not provide for overlays. We added a user function that allowed an overlay to be called in and run from the magnetic tape unit. This overlay performs the data acquisitions from the synchronous detector and provides a real-time display of the accumulating data. When preset limits are reached, the data are recorded on magnetic tape and control is returned to the FOCAL program. The FOCAL program then reads the data as required from the magnetic tape and another user function displays the data on a 10-in. oscilloscope screen. A cursor is moved by the operator to select the peaks used in the reduction. In addition to these programs, we used another FOCAL program to iterate the sensitivity ratio calculations and a FOCAL least-squares program to fit the data to straight lines.

Experimental Procedure

The procedure was modified somewhat during the course of the study. The method discussed here was used for the last three experiments.

Before any experimental series was begun, we tuned up the quadrupole mass filter system to its optimum performance, adjusting the electron bombardment voltage to 18 V so that only parent ions of the water species were produced and adjusting the resolution so that the peaks accumulated by the data system were well-resolved. Once this adjustment was made, the power supplies, except for the electron multiplier voltage, were left on to minimize drift. Since vibration from the rotating chopper caused the capacitance

manometers to drift, each manometer was mechanically isolated from the apparatus frame to minimize this effect.

It was desirable to sample the gas in each inlet system as often as possible but this was limited by the time necessary to pump out the preceding sample. We found the following procedure satisfactory. The first sample was admitted to inlet system 1 (H_2O) and a constant pressure of 0.200 Torr established. The accumulation of the H_2O spectrum, including masses 18, 19, and 20, was begun simultaneously with the starting of a time clock. The accumulation of each spectrum was continued for 5 min with 54 sweeps per accumulated spectrum. The next sample was then put into inlet system 2 (mixture of H_2O , HDO , and D_2O) and adjusted to a constant pressure of 0.200 Torr while sample number 1 was pumped out. The pumpout of system 1 was continued for fifteen minutes to reduce the possible cross talk between systems 1 and 2. Twenty minutes after the clock started, the accumulation of the mass spectrum of the mixture began. After 5 min, it was terminated and the whole procedure repeated for inlet system 3 (D_2O). The cycle was repeated continuously all day without interruption. We found an interruption of 1-2 h decreased the precision of the measurements. The procedure produced more precise results than one in which an inlet system was pumped out for 10 min before the sample was put into the next inlet system.

Data Analysis

The data from the computer-analyzed mass spectra (the intensities) were in the form of the sum of counts of masses 18, 19, and 20 (corrected for background) for each experimental point. In addition, the time at which the

analysis of each sample was begun was recorded and the total pressure of each sample was measured. These data are used to calculate the sensitivities of the water species.

The sensitivity of water, using the data points obtained from inlet system 1, is given by

$$S_{H_2O} = \frac{N_{18}}{P_1 - \frac{N_{19}}{S_{HDO}} - \frac{N_{20}}{S_{D_2O}}}, \quad (4)$$

where N_{18} , N_{19} , and N_{20} are the numbers of counts in the corresponding mass peaks and P_1 is the total sample pressure in inlet system 1.

For the data from inlets 2 and 3 we write the following two equations:

$$S_{HDO} = \frac{N_{19}}{P_2 - \frac{N_{18}}{S_{H_2O}} - \frac{N_{20}}{S_{D_2O}}} \quad (5)$$

and

$$S_{D_2O} = \frac{N_{20}}{P_3 - \frac{N_{18}}{S_{H_2O}} - \frac{N_{19}}{S_{HDO}}}, \quad (6)$$

where P_2 and P_3 are the total pressures in inlet systems 2 and 3. In all three equations, the terms following the total pressures represent the partial pressures of the impurity species in that sample.

Unfortunately, as the equations show, the sensitivity of the other two species must be known to calculate the sensitivity of the first. It was necessary, therefore, to use an iterative technique. A computer code was

programmed to calculate S_{H_2O} at each timed interval, assuming that the corrections to the total pressure were negligible. Then it was assumed that $S_{H_2O} = S_{HDO} = S_{D_2O}$ to correct the total pressures in the first iteration. The program fit each sensitivity curve as a function of time by the linear least-squares technique. In the second and subsequent iterations, the S_{H_2O} , S_{HDO} , and S_{D_2O} values from the previous iterations were used to make the corrections to the total pressures, again fitting each sensitivity-vs-time plot by the linear least-squares method. At the end of each cycle, the program calculated the sensitivity ratio at times of 0, 75, 150, 225, 300, 375, and 450 min. The iterations continued until the sensitivity values and the ratio reached constant values. This convergence usually occurred within five iterations.

RESULTS AND DISCUSSION

The underlying assumption of this project is that the sensitivity measured in any one of the three inlet systems can be directly related to the sensitivities measured in either of the other two. We did not really anticipate that the sensitivities measured in each system would be equal since it is difficult to make leaks as small as 13×10^{-3} cm identical, but we did expect that the three systems could be calibrated against each other. Figure 4 shows one of the measurements used to calibrate the three gas inlet systems against each other. The sensitivity of H_2O was measured periodically in each of the three inlet systems and seems to change linearly with time. The measured sensitivities in each inlet system are different but have nearly

parallel relationships. In the first three sensitivity calibration experiments, all lines are nearly parallel and show a positive trend. The latter was not always true, however. In later experiments, we saw both small positive and negative slopes. In calibration experiments 1, 2, and 3, we fitted the points to straight lines by the least-squares method and took the sensitivity ratios at specified times. The averages are shown in Table 2. The agreement among experiments 1, 2, and 3 is excellent.

At a later time, after all the experiments on sensitivity were run, we rechecked the intercalibration factors of the inlet systems and found that the ratio inlet 1/inlet 3 had changed for some unknown reason. These data are shown as experiments 4, 5, and 6 in Table 2. It was apparent, therefore, that a method must be devised to check the inlet system correction factors simultaneously during each experiment which measured S_{H_2O} , S_{HDO} , and S_{D_2O} . We discovered that the ratio of the sums of the counts for all three peaks in each inlet system for each measurement of S_{H_2O} , if plotted as a function of time, gave the same result as measuring the S_{H_2O} from the mass 18 peak alone. That is, the ratios

$$\frac{(N_{18} + N_{19} + N_{20})_{\text{inlet 1}}}{(N_{18} + N_{19} + N_{20})_{\text{inlet 3}}} = \frac{S_{H_2O} \text{ inlet 1}}{S_{H_2O} \text{ inlet 3}} \quad (7)$$

and

$$\frac{(N_{18} + N_{19} + N_{20})_{\text{inlet 2}}}{(N_{18} + N_{19} + N_{20})_{\text{inlet 3}}} = \frac{S_{H_2O} \text{ inlet 2}}{S_{H_2O} \text{ inlet 3}} \quad (8)$$

are equal. The ratios from the left side of eqs. (7) and (8) for experiments 4, 5, and 6 are shown in parentheses in Table 2 for comparison. (The data for experiments 1, 2, and 3 are not available.) Thus, it was possible to calculate inlet system intercalibration factors for each individual experiment designed to measure S_{H_2O} , S_{HDO} , and S_{D_2O} as well as to account for day-to-day changes in the sensitivity-vs-time behavior. These calibration factors measured using the sum-of-counts method in each experiment are given in Table 3. It is interesting that the calibration factors measured in the S_{H_2O} , S_{HDO} , and S_{D_2O} experiments do not agree with either set (before and after) of calibration experiments, but do agree with each other. Furthermore, if the sensitivity experiments are corrected with the inlet system correction factors from the calibration experiments, the sensitivity curves for S_{H_2O} , S_{HDO} , and S_{D_2O} are inconsistent; whereas if the data are corrected with the individual calibration factors from each H_2O , HDO , and D_2O sensitivity experiment, they are. This is illustrated in Fig. 5.

Figure 5A shows the data from sensitivity experiment E. Sensitivity, S_i , where i is H_2O , HDO , or D_2O , is plotted vs time using the correction factors from the first calibration experiments. The line for S_{H_2O} is displaced from the lines for S_{HDO} and S_{D_2O} . In Fig. 5B, however where the sensitivity curves are corrected using the correction factor determined in the same experiment, E, the lines for S_{H_2O} , S_{HDO} , and S_{D_2O} are approximately the same. The above result gives further support for the use of ΣNi values measured in each sensitivity experiment to calculate the correction factor rather than the values determined in the calibration experiments.

Equation (3) shows that to obtain the values of the equilibrium constant, K_{HDO} , both the intensity ratio and the sensitivity ratio must be measured. We measured the intensity ratio separately in the inlets systems, partly to illustrate the independence of these values from the inlet system.

The results of the intensity ratio measurements at $26.3 \pm 0.4^\circ\text{C}$ are given in Table 4. Note that the intensity ratios measured in each of the three inlet systems are the same, especially if cycle 4 in inlet 2 is ignored. The average of all three sets of data is $I = 3.81 \pm 0.09$ in which the listed deviation is the standard deviation of a single measurement. The standard deviation of the mean is ± 0.01 . These measurements agree very well with those in Ref. [5] but disagree with those in Refs. [1-4]. (See Table 1.)

Six separate experiments were conducted measuring the sensitivities of H_2O , HDO , and D_2O as a function of time. As mentioned previously, these sensitivities were iterated until they were constant. The results for each experiment are shown in Fig. 6. Each sensitivity was fitted by the least-squares method to a straight line. Qualitatively, the results show that the sensitivities are approximately equal within the scatter of the data. In particular, the three experiments with the least experimental scatter (Experiments B, E, and F) show that the sensitivities are not only equal (within the scatter) but are nearly constant.

The iteration computer code also calculated the sensitivity ratio, S_i , at seven different times. The ratios are shown in Table 5. Again, the sensitivity ratio obtained is approximately one. These values of S_i , where i designates the experiment (A-F), are plotted in Fig. 7. The surprising result

is that the sensitivity ratio in each experiment is a linear function of time. This is unexpected since S should be constant and may indicate the presence of yet another systematic error in the data.

There is another aspect of the data that should be mentioned. A slightly different procedure was used in the last three experiments (D, E, and F), as mentioned previously. The next sample was put into the inlet system at the same time as the previous sample was being pumped out. In experiments A, B, and C, we waited 10 min while pumping out the previous sample before adding the next sample. The plots in Fig. 7 all have positive slopes and less experimental scatter as a group than the plots for experiments A, B, and C. (The experimental scatter correlates with the absolute slope; a large slope indicates more experimental scatter.)

The presence of the systematic error and the general increase in precision by the change in procedure suggest that further experiments should be done; however, funds for the continuation of this work are not available.

CONCLUSIONS

Inasmuch as it is apparent that more work is required, we feel that the interpretation of the data should be restricted. Our best estimate based on the plots in Fig. 6 is that the sensitivities of H_2O , HDO , and D_2O are probably equal and constant. This implies that the sensitivity ratio S is constant and equal to unity. We have not shown this conclusively, however, and there is a lot of scatter in the data. Nevertheless, we would predict that $K_{HDO} = S \cdot I = 3.81 \pm 0.06$.

On the other hand, a detailed analysis of the sensitivity ratio data shows that S is a function of time, which implies a systematic error in the data. Correcting a limited set of experimental points for this time dependence leads to a value of $K_{\text{HDO}} = 3.69$ (see Appendix).

The theory of isotopic exchange reactions [6-8] predicts a value of $K_{\text{HDO}} = 3.85$ at 25°C . Unfortunately, we cannot unambiguously confirm the theory on the basis of the present work. However, in previous tests of the theory using isotopic self-exchange reactions (NH_3 [10], H_2S [3,7], H_2Se [3,7], and the tritiated water reactions [5]) the intensity ratios agreed with the theoretical equilibrium constant. It is hoped that this paper might stimulate others to devise a method to test the theory with more precision.

ACKNOWLEDGMENTS

We wish to thank John Magistad of JGM Associates for his suggestions, relative to the statistical analysis of the data, that led to the discovery of the time dependence of S . We also thank James Cormier for help in the construction of the apparatus, and R.S. Newbury for critically reviewing the manuscript.

This work was performed under the auspices of the U.S. Energy Research & Development Administration under contract no. W-7405-Eng-48.

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APPENDIX

Since we have intensity ratios as a function of time from the measurements of S_{HDO} from inlet system 2 for experiments D, E and F, we can combine these with the measurement of S to calculate an equilibrium constant. These data are given in Table 6. The intensity ratios are at the lower end of those measured previously and agree with those in Refs. [1-4] rather than those in Ref. [3]. The value of K calculated using these data is 3.69. We are reluctant to conclude, however, that this is the correct value of K because of the systematic error.

TABLE 1
Intensity Ratios

I	Temp (°C)	Ref.
3.76 ± 0.02	25	1
3.74 ± 0.07	25	2
3.76 ± 0.03	24	3
3.76 ± 0.08	23	4
3.82 ± 0.05	23	5

TABLE 2

Comparison of S_{H_2O} in Inlet Systems 1, 2, and 3

Experiment	Inlet 1/Inlet 3	Inlet 2/Inlet 3
1	1.077	0.799
2	1.081	0.800
3	1.093	0.799
4	1.114 (1.116)	0.792 (0.792)
5	1.117 (1.111)	0.802 (0.800)
6	1.109 (1.109)	0.806 (0.809)

TABLE 3

Calibration Factors Used in the Sensitivity Measurement Experiments

Experiment	$\frac{(\sum N_1)}{1}$ Inlet 1	$\frac{(\sum N_1)}{1}$ Inlet 2
	$\frac{(\sum N_1)}{1}$ Inlet 3	$\frac{(\sum N_1)}{1}$ Inlet 3
A	1.159	0.816
B	1.193	0.818
C	1.179	0.813
D	1.178	0.813
E	1.196	0.819
F	1.186	0.814

TABLE 4

Comparison of Intensity Ratios (I) as Measured at $26.3 \pm 0.4^\circ\text{C}$ in Inlet Systems

Cycle	$I_{\text{Inlet 1}}$	$I_{\text{Inlet 2}}$	$I_{\text{Inlet 3}}$
1	3.87	3.82	3.75
2	3.78	3.79	3.99
3	3.82	3.71	3.74
4	3.73	4.35	4.16
5	3.82	3.85	3.80
6	3.77	3.80	3.75
7	3.80	3.78	3.77
8	3.86	3.80	3.76
9	3.78	3.79	3.76
10	3.79	3.80	3.77
11	3.71	3.79	3.79
12	3.83	3.97	3.73
13	3.98	3.83	3.75
Averages	3.81	3.85	3.81
Standard Deviation	± 0.07	± 0.15	± 0.13
Average without Cycle 4		3.81	
Standard Deviation		± 0.06	

TABLE 5

Sensitivity Ratio S_i as a Function of Time

(i = Experiment A-F)

Time (min)	S_A	S_B	S_C	S_D	S_E	S_F
0	0.89 ₅	1.02 ₁	1.05 ₁	0.97 ₄	0.99 ₁	0.98 ₅
75	0.92 ₆	1.01 ₃	1.02 ₆	0.97 ₆	0.99 ₄	0.99 ₁
150	0.95 ₉	1.00 ₄	1.00 ₁	0.97 ₈	0.99 ₆	0.99 ₇
225	0.99 ₂	0.99 ₆	0.97 ₇	0.98 ₀	0.99 ₈	1.00 ₃
300	1.02 ₇	0.98 ₈	0.95 ₃	0.98 ₁	1.00 ₁	1.00 ₉
375	1.06 ₃	0.98 ₀	—	0.98 ₃	1.00 ₃	1.01 ₆
450	1.09 ₉	—	—	0.98 ₅	—	1.02 ₂

TABLE 6

Values of I, S, and K_{HDO} for Experiments D, E, and F

Experiment	Time (min)	I	S	K_{HDO}
D	21	3.78	0.975	3.68
D	80	3.71	0.976	3.62
D	140	3.80	0.978	3.71
D	210	3.81	0.979	3.73
D	280	3.53	0.981	3.47
D	340	3.77	0.982	3.70
D	410	3.66	0.984	3.60
Averages		3.72		3.64
E	20	3.79	0.992	3.76
E	80	3.67	0.994	3.65
E	150	3.73	0.996	3.71
E	221	3.73	0.998	3.73
E	280	3.67	0.999	3.66
E	340	3.55	1.001	3.55
Averages		3.69		3.68
F	20	3.98	0.986	3.92
F	80	3.66	0.991	3.63
F	140	3.70	0.996	3.69
F	215	3.84	1.002	3.84
F	280	3.65	1.008	3.68
F	340	3.70	1.012	3.75
F	400	3.61	1.018	3.67
Averages		3.73		3.74
Overall Averages		3.71		3.69

FIGURE 1. LEGENDS

Figure 1. Gas inlet system.

Figure 2. Molecular leaks.

Figure 3. Total mass 18 signal showing chopped beam.

Figure 4. Comparison of gas inlet systems.

Figure 5. Examples of plots of S_i vs time in which $i = \text{H}_2\text{O} = \bigcirc$, $\text{HDO} = \Delta$, or $\text{D}_2\text{O} = \square$, with correction factors from A: first calibration experiments and B: experiment E.

Figure 6. Plots of S_i vs time (experiments A-F) in which $i = \text{H}_2\text{O} = \bigcirc$, $\text{HDO} = \Delta$, or $\text{D}_2\text{O} = \square$.

Figure 7. Plots of S_i vs time in which $i =$ experiments A-F.

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Pyper - Fig. 1

Pyper - Fig. 2

Pyper - Fig. 3

Pyper - Fig. 4

Pyper - Fig. 5

Pyper - Fig. 6

Pyper - Fig. 7