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Diode Laser Measurements of Air and Nitrogen Broadening in the ν_2 Bands of HDO, $H_2{}^{16}O$, and $H_2{}^{18}O$

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Pressure-broadening coefficients for several rotation–vibration lines in the ν_2 bands of HDO, $H_2{}^{16}O$, and $H_2{}^{18}O$ have been determined from laboratory spectra recorded in the 1260- to 1360-cm^{-1} region with a tunable diode laser spectrometer system. Air and nitrogen were used as the broadening gases and, for all the measured transitions, the nitrogen-broadened half-widths were found to be consistently larger than the corresponding air-broadened half-widths by about 12%. The results have been compared to previously published values when appropriate.

INTRODUCTION

High-resolution measurements consisting of line positions, intensities, and half-widths in selected spectral regions in the ν_2 bands of H_2O and HDO have been published in the recent past (*1–11*). Some of these studies have been performed using tunable diode lasers (*1, 2, 7, 9, 10*). Although the high resolution and high sensitivity of diode lasers are well suited for obtaining very-high-quality data, the narrow tunability of diodes limits the amount of data that can be obtained in any one study. Therefore, in this work we report additional diode laser measurements of air- and nitrogen-broadened half-widths for several lines in the ν_2 bands of HDO and H_2O ($H_2{}^{16}O$ as well as $H_2{}^{18}O$) in the 1260- to 1360-cm^{-1} spectral region, with primary emphasis on HDO.

EXPERIMENTAL DETAILS

The diode laser spectrometer used in this work has been described in detail previously (*12, 13*). All measurements were obtained with a 50-cm absorption path pyrex cell fitted with Teflon valves and wedged potassium chloride windows. Data were collected on a Hewlett-Packard X–Y plotter for later analysis. The data reduction procedure has been detailed in Refs. (*12, 13*).

The HDO samples were prepared by mixing high-purity research grade water (Burdick & Jackson Laboratories, Inc., Michigan) and 99.5 mole% deuterium oxide

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(Matheson Coleman & Bell, Division of the Matheson Company, Inc., N.J.). Three different samples of HDO were prepared with varying initial amounts of H_2O and D_2O. These various samples were used especially for checking consistency in our line intensity measurements, data which were also obtained along with half-width measurements. However, in this work, results pertaining only to line half-widths will be reported. Accurate values for the initial amounts of H_2O and D_2O were determined using a Mettler Model mechanical–analytical balance accurate to 0.01 mg. Because both samples were measured and mixed at room temperature, no corrections were made to their observed weights. The partial pressures of HDO, H_2O, and D_2O in the resulting mixture were calculated using the equilibrium constants of Bruce and Jelinek (*14*). A few cubic centimeters of these mixtures were introduced into separate cold fingers which were easily attached or removed from the absorption cell and vacuum manifold using O-ring ball joints. The 0- to 10- and 0- to 100-Torr pressure heads were connected to the system so that sample pressures could be monitored continuously while recording the data. The pressures were read on Datametrics Model 1174 barocel electronic manometers. Sample temperatures were monitored using a thermocouple junction attached to the cell wall and were read on a Fluke model digital voltmeter.

ANALYSIS

An effective Doppler half-width b'_D for each line was determined from spectra recorded at two or more low pressures of HDO (or H_2O). After recording these low-pressure scans, the sample was pumped out. A fresh sample was introduced into the cell, and either air or nitrogen was added until total sample pressures reached 20 to 60 Torr. Because the partial pressures of samples varied between 0.1 and 2 Torr, broadening caused by HDO, H_2O, and D_2O molecules present in the sample was taken into consideration while deriving the air-broadened or nitrogen-broadened half-widths. Therefore, the Lorentz broadening coefficient, b_L, was computed using

$$b_L = b_L^0(\text{HDO-HDO})p(\text{HDO}) + b_L^0(\text{HDO-H}_2\text{O})p(\text{H}_2\text{O}) + b_L^0(\text{HDO-D}_2\text{O})p(\text{D}_2\text{O}) + b_L^0(\text{HDO-air})p(\text{air}), \quad (1)$$

where the various symbols have their usual meanings. A nominal value of 0.35 cm^{-1} atm^{-1} was assumed for b_L^0(HDO-HDO), b_L^0(HDO-H_2O), and b_L^0(HDO-D_2O). Half-widths were deduced by the method described previously (*12, 13*). This procedure also included corrections to measured half-widths due to absorptions in line wings (*15*), which varied from <1 to 6%.

RESULTS

Table I summarizes the results obtained for 32 ν_2-band lines of HDO. The values given in parentheses are the standard deviations of all of the measurements in units of the last digit. These results were obtained from three or more scans at three or more different broadening pressures. Assignments and line positions were taken from the work of Guelachvili (*11*). The half-widths presented in this table are the only experi-

TABLE I

Air- and N_2-Broadened Half-widths (in cm^{-1} atm^{-1}) for Selected Lines in the ν_2 Band of HDO at 296 K

Wavenumber (cm^{-1})	J' K_a' K_c'	J'' K_a'' K_c''	Halfwidth			$b_L^o(N_2)$ / $b_L^o(Air)$
			Air-Broadened		N_2-Broadened	
			AFGL 1982†	Present Study		
1260.423180	4 2 2	5 3 3	0.0910	0.0865(9)	0.0973(15)	1.12
1279.951129	8 2 7	9 2 8	0.0740	0.0790(12)	0.0942(8)	1.19
1280.554435	8 0 8	9 1 9	0.0660	0.0593(12)	0.0703(9)	1.19
1280.696312	6 1 5	7 2 6	0.0880	0.0889(24)	0.0992(15)	1.12
1281.264213	7 2 5	8 2 6	0.0910	0.0869(5)	0.0932(6)	1.07
1281.454881	8 1 8	9 1 9	0.0660	0.0588(5)	0.0674(3)	1.15
1281.817685	8 1 8	9 0 9	0.0660	0.0620(10)	0.0693(24)	1.12
1284.898233	7 1 6	8 1 7	0.0900	0.0896(12)	0.1005(19)	1.12
1287.639176	2 2 1	3 3 0	0.0920	0.0907(28)	0.1016(8)	1.12
1288.018826	2 2 0	3 3 1	0.0910	0.0852(7)	0.0968(11)	1.14
1292.959802	7 3 4	8 3 5	0.0900	0.0798(13)	0.0874(11)	1.10
1294.920730	7 1 7	8 1 8	0.0760	0.0722(10	0.0820(6)	1.14
1298.156738	7 3 5	8 3 6	0.0810	0.0732(17)	0.0796(14)	1.09
1306.810183	6 0 6	7 0 7	0.0870	0.0783(8)	0.0885(9)	1.13
1309.662605	6 1 6	7 0 7	0.0850	0.0840(27)	0.0901(16)	1.07
1315.006658	4 3 2	4 4 1	0.0770	0.0770(14)	0.0890(6)	1.16
1315.086796	9 2 8	9 3 7	0.0730	0.0708(16)	0.0797(10)	1.13
1315.190842	4 3 1	4 4 0	0.0790	0.0824(12)	0.0920(19)	1.12
1318.112742	6 3 3	6 4 2	0.0830	0.0783(16)	0.0889(14)	1.14
1319.433545	5 0 5	6 0 6	0.0930	0.0860(8)	0.0958(8)	1.11
1325.662204	8 3 5	8 4 4	0.0860	0.0739(16)	0.0865(13)	1.17
1325.822899	6 4 3	7 4 4	0.0690	0.0722(16)	0.0850(17)	1.18
1326.031366	1 1 1	2 2 0	0.0980	0.1044(31)	0.1109(28)	1.06
1326.357683	7 2 6	7 3 5	0.0830	0.0805(13)	0.0868(23)	1.08
1328.096881	4 0 4	5 1 5	0.0950	0.0936(12)	0.1000(20)	1.07
1328.273850	5 3 3	6 3 4	0.0810	0.0761(9)	0.0857(6)	1.13
1333.654835	4 2 3	4 3 2	0.0890	0.0912(19)	0.1007(9)	1.10
1334.277049	3 2 2	3 3 1	0.0890	0.0905(19)	0.1026(27)	1.13
1336.856994	5 1 5	5 2 4	0.0930	0.0868(9)	0.0970(20)	1.12
1339.392090	4 1 4	5 0 5	0.0950	0.0907(16)	0.1008(11)	1.11
1342.286233	5 2 3	5 3 2	0.0910	0.0887(12)	0.1033(22)	1.16

†Ref. (16).

mental results available for these lines. Hence no comparisons could be made with other published values, except that the measured air-broadened half-widths are compared with the calculated air-broadened half-widths listed in the 1982 Air Force Geophysics line parameters compilation (*16*). Comparisons between these two sets show that measured half-widths are slightly smaller than the calculated values in most of the cases. For all the lines reported in this table, we find that nitrogen-broadened half-widths are larger than the air-broadened half-widths, and their ratio computed for each line and listed in the last column of this table gives a value of about 1.12. On average, we find that $b_L^0(N_2)/b_L^0(\text{air})$ is 1.12 ± 0.03.

In Table II, we list the results obtained for several ν_2-band lines of $H_2{}^{16}O$ and $H_2{}^{18}O$. As for HDO, these measurements were obtained from three or more scans at three or more broadening pressures. It may be noted that for these measurements, samples of HDO were used and therefore the absorptions were due to the fractional part of H_2O in the resulting mixture (25–50%). Air-broadened half-widths determined from this study are compared with calculated values given in Ref. (*16*). Wavenumbers and assignments of lines listed in this table were taken from Ref. (*11*). Contrary to the HDO half-widths, no systematic pattern was observable between the experimental

TABLE II

Air-, N_2-, and Self-Broadened Half-widths (in cm^{-1} atm^{-1}) for Some Lines in the ν_2 Bands of $H_2{}^{16}O$ and $H_2{}^{18}O$ (at 296 K)

Wavenumber (cm^{-1})	J' K'_a K'_c	J'' K''_a K''_c	Halfwidth: Air-Broadened, AFGL 1982†	Halfwidth: Air-Broadened, Present Study	Halfwidth: N_2-Broadened	Halfwidth: Self-Broadened	$b^o_L(N_2)/b^o_L(Air)$
1267.643133*	5 0 5	6 3 4	0.0742	0.0508(5)	0.0581(10)		1.14
1267.953295	10 4 6	11 5 7	0.0752	0.0547(6)	0.0650(11)		1.19
1280.047808	9 4 5	10 5 6	0.0749	0.0606(13)	0.0692(6)		1.14
1282.806502*	8 4 5	9 5 4	0.0614	0.0957(7)	0.1074(21)		1.12
1287.400386	8 4 5	9 5 4	0.0620	0.0933(4)	0.1026(21)		1.10
1308.179228	7 3 5	8 4 4	0.0764	0.0637(31)	0.0744(6)	0.3494(64)	1.17
1308.461489*	{ 7 5 3	8 6 2	0.0498	0.0794(8)	0.0903(13)		1.14
	{ 14 1 13	15 2 14	0.0113				
1308.634514*	7 5 2	8 6 3	0.0518	0.0801(17)	0.0903(11)		1.13
1309.59400*	4 0 4	5 3 3	0.0850	0.0863(8)	0.0929(6)		1.08
1311.043203*	{ 7 6 2	8 7 1	0.0375	0.0576(9)	0.0670(13)	0.2495(50)	1.16
	{ 7 6 1	8 7 2	0.0374				
1313.483387	4 0 4	5 3 3	0.0858	0.0860(6)	0.0955(24)	0.4100(104)	1.11
1339.519163	6 4 2	7 5 3	0.0639	0.0870(8)	0.0985(15)		1.13
1340.167084	7 3 4	8 4 5	0.0848	0.0935(8)	0.1018(16)		1.09
1378.493420	7 1 6	7 4 3	0.0730	0.0877(8)	0.1005(8)	0.4190(109)	1.15

†Ref. (16).
*$H_2{}^{18}O$ transitions.

and theoretical air-broadened half-widths. Nevertheless, N_2-broadened half-widths are approximately 12% larger than corresponding air-broadened half-widths, which is evident from the ratios given in the last column. In addition to air- and N_2-broadened half-widths, a few self-broadened half-widths have also been measured, and those results are also given in this table.

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