H_2O self-broadening coefficients of rotation-vibration lines in the 15 500 – 16 000 cm^{-1} region

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ABSTRACT

Line broadening coefficients of the H_2O-H_2O system were investigated in the region 15500 – 16000 cm^{-1} using a high resolution Fourier-transform spectrometer IFS-125M. The White type multipass absorption cell with a basic length of 60 cm was used. Least-square-fitting algorithm WXSPE was used to retrieve of the spectroscopic parameters from measured spectral data set. Calculations of self-broadening are performed using a semi-empirical approach. This method is further developed by using anharmonic wavefunctions in the estimates of line profiles. This approach explicitly takes into account all scattering channels induced by collisions. Calculated data are in a good agreement with the measured ones.

Keywords: Fourier-transform spectrometer, high luminance light-emitting diode, broadening coefficient, semi-empirical calculations

1. INTRODUCTION

It was earlier shown[1-3] that the use of high luminance light-emitting diode (LED) emitters as the light sources in Fourier-transform spectrometers permits one to enhance their threshold sensitivity in the visible range by orders of magnitude. The purpose of this research is to investigate thoroughly the $H_2{}^{16}O$ line self-broadening in the 16 630 – 17 030 cm^{-1} range recorded by a Fourier-transform spectrometer using the high luminance LEDs as light sources.

2. EXPERIMENT

Experiments have been conducted using the CREE XPE AMB-L1-A30-M3-D-01 LED as light sources because of their high luminance in the range of ~ 17 000 cm^{-1}. The LEDs used in our experiment have the power of 1.5 W, fed from the power unit GPR-30600 which has ensured the voltage instability of 0.1 mV with the current instability of less than 4 mA. The spectra width of the diode radiation is 700 cm^{-1}. In these conditions, the LED radiation has provided an increase of the signal amplitude at 17 000 cm^{-1} by over 2.5 times as compared to the halogen lamp radiation. In addition, the noise, when using a LED, turns out to be 3 times less than the noise produced by a halogen lamp. Thus, the present spectrometer demonstrates an 8-9 time increase in the efficiency of the light source as compared to the system based on a halogen lamp. The maximum signal, which provides the required signal-to-noise ratio, has been observed on the path length L = 24 meters. Having made 7776 co-added scans, we have been able to obtain a (S/N)-ratio of 10 000 which corresponds to a minimum absorption coefficient K_{th} =1.2×10^{-8} cm^{-1}.

In this research, the spectra were recorded using a multipass White cell with a base length of 60 cm, which was connected with a Bruker IFS 125M Fourier-transform spectrometer and filled by $H_2{}^{16}O$ vapor to the pressure of 8 and 27 mbar. Triangular apodization has been used with the spectral resolution equal to 0.05 cm^{-1}. The design of the multipass vertical absorption cell (60 cm long and a volume of 22 liters) is based on the White's three-mirror configuration.

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Pressure measurements have been performed by the AIR-20M pressure transducer with the pressure measurable range 0 -100 kPa and an accuracy of the order of 0.1%. Temperature in a 75 m^3 measurement room has been stabilized by the *Midea MSE-24HR* air conditioner with an error better than 1K, permitting long-time (up to 9 days) spectrum measurements.

The radiation after the multipass cell was input to the Fourier spectrometer through the emission channel. The *IFS-125M* Fourier transform spectrometer was not put under vacuum. Low air humidity (relative humidity no more than 20%) allowed us to avoid purging the spectrometer with dry nitrogen.

Three water vapor spectra were recorded at following conditions (Table 1).

Table 1. Experimental conditions.

№	Sample pressure (H_2O), mbar	Temperature, K	Path length, cm
1	8	297	2400
2	16,5	297	2400
3	27	297	2400

The line search and determination of water vapor line parameters were carried out by using the automated program system described previously[4]. Briefly, line search was performed using algorithms of pattern recognition theory, and lines parameters were fitted one by one to a Voigt profile convolved by the instrumental function. In the cases of overlapping lines all parameters were determined simultaneously. Fitting procedure allows also automatic determination of base line. Halfwidths of 16703.92 cm^{-1} water vapor line at different pressures are shown in Fig. 1.

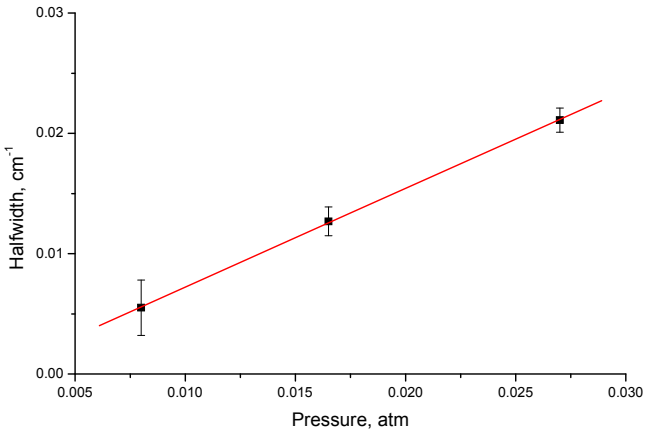

Fig. 1. Pressure dependence of self-broadening of the 16703,92 cm^{-1} water vapor line.

3. DETAILS OF CALCULATION AND RESULTS

Self-broadening coefficients of vibration-rotation lines of water molecules are calculated using a semi-empirical method[5]. This approach was successful used for many molecular systems (see, e.g.[6-8]). The method is based on the impact theory of broadening, modified through including additional parameters obtained by involving empirical data. Model parameters are determined by fitting the line broadening and shift coefficients on experimental data. This method was further developed by using anharmonic wavefunctions[9] in the estimates of the water vapor line parameters. Results of these calculations demonstrate improved agreement between observed and calculated parameters for both the line widths and the line shifts. The main feature is the use of a complete set of high accuracy vibration-rotation dipole transition moments calculated for all possible transitions using

wavefunctions determined from va riational nuclear motion calculations and an *ab initio* dipole moment surface.

The main contribution to the self-broadening of water vapor line is made by the dipole-dipole interaction. We also take into account the higher-order electrostatic (dipole-quadrupole, and quadrupole-dipole) interactions and polarization (induction and dispersion) interactions. To take into account the contributions of different scattering channels, corresponding to collisional transitions, we used the transition probabilities $D^2(ii'|l)$ and $D^2(ff'|l)$, reconstructed from Einstein coefficients in line list BT2[10]. The cut procedure is applicable for molecules, characterized by strong interactions, when the distance of the closest approach of molecules is less than the interruption parameter b_0. The interaction of two strong dipoles (H_2O–H_2O) ensures fulfillment of this condition; the influence of short-range forces is weak in this case and is accounted for via the correction factor. All the calculations were made for the temperature $T = 297$ K.

We performed the calculations of self-broadening coefficients of water vapor lines for 4 absorption bands: $3\nu_1+2\nu_2+\nu_3$, $4\nu_1+2\nu_2$, $4\nu_1+\nu_3$ and $5\nu_1$. One set of semi-empirical parameters (with a correction factor $C_l = c_1/(c_2\sqrt{J+1})$ considering in a simple manner the J-dependence of the efficiency function) describes line widths in all four bands: c_1=1.22, c_2=0.2; the gas kinetic diameter was kept 10.0 Å (as for ~13000cm^{-1}). Figure 1 presents the calculated and experimental[11,12] self-broadening coefficients for above mentioned absorption bands[11] and $3\nu_1+1\nu_3$, $2\nu_1+2\nu_2+\nu_3$ bands[12] (N is the number of vibration-rotation transitions). It is seen that the calculations are in satisfactory agreement with experiment. The root-mean-square (RMS) deviations of our data from literature values[11,12] are presented in Table 2. The full set of experimental and theoretical data is given in Table 3.

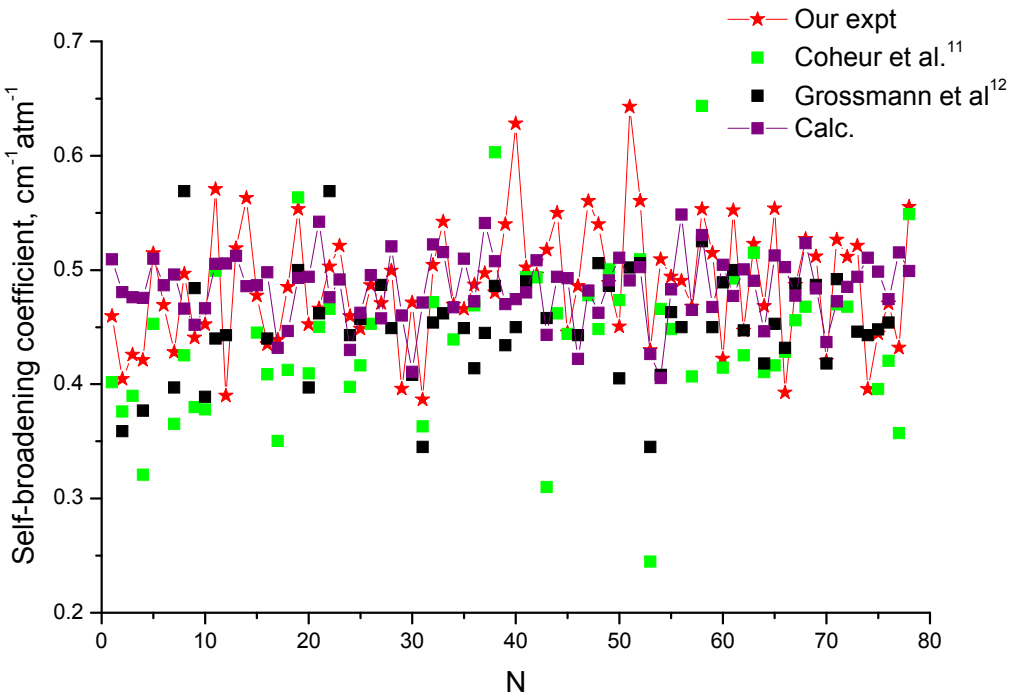

Fig. 2. Comparison of calculated and measured [11,12] self-broadening coefficients.

Table 2. The root-mean-square (RMS) deviations (in cm-1atm-1) of our experimental/theoretical values from experimental data[11,12].

Reference	RMS (Our expt-Ref.), $cm^{-1}atm^{-1}$	RMS (Our calc.-Ref.) , $cm^{-1}atm^{-1}$
Coheur et al. [11]	0.0569 [11.2%]	0.0691 [13.7%]
Gr-Br [12]	0.0608 [11.0%]	0.0589 [10.9%]
This paper (calculations)	0.0566 [9.2%]	

Table 3. $H_2{}^{16}O$ self-broadening coeffcients γ and their uncertainties U (for measured values) at the reference temperature 296 K.

№	Frequency, cm^{-1}	Intensity, cm/mol	$(v_1\ v_2\ v_3)^{up}$	$(J\ K_a\ K_c)^{up}$	$(J\ K_a\ K_c)^{low}$	γ^{expt}, $cm^{-1}atm^{-1}$	U, $cm^{-1}atm^{-1}$	γ^{calc}, $cm^{-1}atm^{-1}$
1	16636.13279	1.945E-25	3 2 1	6 1 5	7 1 6	0.459	0.068	0.509
2	16649.14794	1.945E-25	3 2 1	6 0 6	7 0 7	0.405	0.078	0.480
3	16651.32464	1.263E-25	3 2 1	5 2 3	6 2 4	0.426	0.064	0.476
4	16654.74410	1.935E-25	3 2 1	5 4 2	6 4 3	0.421	0.090	0.475
5	16669.44069	4.281E-25	3 2 1	5 2 4	6 2 5	0.515	0.102	0.510
6	16681.39532	1.815E-25	4 2 0	5 0 5	6 1 6	0.469	0.078	0.487
7	16684.31056	6.357E-25	3 2 1	4 2 2	5 2 3	0.428	0.036	0.496
8	16687.51464	6.317E-25	3 2 1	4 1 3	5 1 4	0.497	0.039	0.466
9	16691.86900	5.415E-25	3 2 1	4 3 1	5 3 2	0.441	0.059	0.452
10	16695.19370	1.805E-25	3 2 1	4 3 2	5 3 3	0.452	0.063	0.466
11	16703.20008	6.638E-25	3 2 1	4 0 4	5 0 5	0.571	0.063	0.505
12	16703.93640	1.233E-25	3 2 1	4 1 4	5 1 5	0.390	0.097	0.506
13	16705.85380	1.110E-25	4 2 0	4 0 4	5 1 5	0.519	0.107	0.512
14	16712.52476	1.040E-25	4 0 1	5 2 3	6 2 4	0.563	0.040	0.486
15	16714.36420	2.968E-25	3 2 1	3 3 0	4 1 3	0.477	0.048	0.486
16	16717.35991	2.868E-25	3 2 1	3 2 1	4 2 2	0.435	0.063	0.498
17	16724.92450	1.775E-25	3 2 1	3 1 2	4 3 1	0.439	0.052	0.432
18	16726.00540	5.364E-25	3 2 1	3 3 1	4 3 2	0.485	0.055	0.446
19	16727.52426	3.209E-25	3 2 1	3 0 3	4 0 4	0.553	0.077	0.493
20	16745.63161	7.460E-25	4 0 1	4 2 2	5 2 3	0.452	0.043	0.494
21	16748.49851	5.374E-25	3 2 1	2 2 0	3 2 1	0.466	0.026	0.542
22	16755.15817	1.033E-24	4 0 1	4 1 3	5 1 4	0.503	0.046	0.476
23	16760.00342	2.447E-25	4 0 1	4 2 3	5 2 4	0.521	0.068	0.492
24	16769.84160	2.617E-25	3 2 1	1 1 0	2 1 1	0.460	0.011	0.430
25	16773.91536	3.469E-25	3 2 1	1 0 1	2 0 2	0.449	0.030	0.463
26	16775.84141	1.293E-25	3 2 1	5 2 4	5 2 3	0.487	0.061	0.496
27	16784.15834	5.876E-25	4 0 1	3 1 2	4 1 3	0.471	0.036	0.457
28	16788.10996	1.053E-24	4 0 1	3 2 2	4 2 3	0.499	0.044	0.521
29	16792.27480	2.116E-25	3 2 1	6 4 2	6 4 3	0.396	0.078	0.460
30	16797.83672	6.427E-25	3 2 1	0 0 0	1 0 1	0.471	0.053	0.411
31	16801.12780	5.745E-25	3 2 1	5 4 2	5 4 1	0.387	0.055	0.471
32	16804.41946	1.875E-24	4 0 1	3 1 3	4 1 4	0.504	0.049	0.522
33	16810.98354	1.003E-24	4 0 1	2 2 0	3 2 1	0.542	0.095	0.516
34	16811.60935	1.354E-25	3 2 1	6 3 3	6 3 4	0.469	0.073	0.467
35	16814.37306	7.941E-25	3 2 1	3 2 2	3 2 1	0.466	0.029	0.510
36	16816.96496	9.124E-25	3 2 1	1 1 1	1 1 0	0.487	0.049	0.473
37	16825.75323	1.815E-24	3 2 1	2 2 0	2 2 1	0.497	0.044	0.541
38	16826.83802	2.507E-25	3 2 1	3 2 1	3 2 2	0.480	0.094	0.508
39	16827.29823	2.567E-24	4 0 1	2 0 2	3 0 3	0.540	0.057	0.470
40	16827.88042	3.329E-25	3 2 1	1 1 0	1 1 1	0.628	0.085	0.474
41	16829.18072	8.904E-25	4 0 1	2 1 2	3 1 3	0.502	0.040	0.480
42	16830.45894	3.770E-25	3 2 1	4 2 2	4 2 3	0.496	0.071	0.508

43	16835.88300	4.973E-25	3 2 1	2 1 1	2 1 2	0.518	0.037	0.443
44	16836.20728	1.885E-25	5 0 0	2 1 2	2 2 1	0.550	0.058	0.494
45	16837.65167	1.093E-25	4 0 1	5 2 4	5 2 3	0.445	0.058	0.493
46	16842.22077	5.976E-25	4 0 1	1 1 0	2 1 1	0.486	0.048	0.422
47	16847.13443	2.547E-25	5 0 0	3 1 2	3 2 1	0.560	0.036	0.482
48	16852.80575	2.015E-24	4 0 1	1 1 1	2 1 2	0.540	0.041	0.463
49	16855.89202	2.216E-25	4 0 1	3 1 3	3 1 2	0.489	0.059	0.491
50	16860.43262	1.213E-25	4 0 1	4 2 3	4 2 2	0.451	0.064	0.511
51	16861.24753	2.777E-25	3 2 1	2 1 2	1 1 1	0.643	0.072	0.491
52	16862.13378	1.634E-25	3 2 1	4 1 3	4 1 4	0.560	0.051	0.502
53	16873.69240	1.324E-25	4 0 1	4 3 2	4 3 1	0.430	0.035	0.426
54	16875.04783	1.835E-24	4 0 1	0 0 0	1 0 1	0.509	0.070	0.405
55	16879.48622	3.519E-25	3 2 1	3 0 3	2 0 2	0.494	0.017	0.483
56	16885.63196	8.483E-25	4 0 1	2 2 1	2 2 0	0.490	0.032	0.549
57	16894.68540	3.820E-25	3 2 1	3 3 0	2 1 1	0.468	0.046	0.465
58	16899.71458	3.209E-25	3 2 1	5 1 5	4 1 4	0.553	0.122	0.531
59	16900.25959	7.971E-25	4 0 1	1 1 0	1 1 1	0.515	0.021	0.467
60	16903.80929	7.681E-25	4 2 0	5 0 5	4 1 4	0.422	0.053	0.505
61	16917.37690	1.845E-25	4 0 1	3 1 2	3 1 3	0.552	0.078	0.477
62	16921.98979	6.638E-25	3 2 1	5 2 4	4 2 3	0.447	0.074	0.500
63	16924.38915	1.845E-25	5 0 0	3 1 2	2 2 1	0.523	0.096	0.490
64	16940.26554	2.757E-24	4 0 1	2 0 2	1 0 1	0.468	0.060	0.446
65	16940.88931	4.151E-25	3 2 1	6 1 5	5 1 4	0.554	0.054	0.513
66	16941.83688	3.038E-25	3 2 1	7 2 6	6 2 5	0.393	0.098	0.502
67	16949.76145	2.056E-24	4 0 1	3 1 3	2 1 2	0.487	0.057	0.478
68	16953.57060	1.043E-24	4 0 1	3 2 2	2 2 1	0.527	0.043	0.523
69	16960.60328	4.863E-25	5 0 0	4 0 4	3 1 3	0.512	0.032	0.484
70	16964.47945	8.052E-25	4 0 1	3 1 2	2 1 1	0.420	0.061	0.437
71	16966.34144	1.404E-24	4 0 1	4 0 4	3 0 3	0.526	0.051	0.472
72	16968.46578	2.025E-24	5 0 0	4 1 4	3 0 3	0.512	0.031	0.485
73	16968.91776	5.675E-25	5 0 0	5 1 4	4 2 3	0.521	0.068	0.494
74	16969.91073	3.429E-25	4 0 1	4 2 3	3 2 2	0.396	0.080	0.511
75	16979.98546	1.303E-24	4 0 1	4 2 2	3 2 1	0.444	0.037	0.498
76	16981.24987	1.725E-24	4 0 1	4 1 3	3 1 2	0.471	0.046	0.475
77	16982.80284	3.519E-25	5 0 0	6 0 6	5 1 5	0.432	0.017	0.515
78	17029.24880	1.073E-25	5 0 0	3 3 0	2 2 1	0.555	0.080	0.499

Self-broadening coefficients for the H_2O molecule are rather big 0.35-0.65 $cm^{-1}atm^{-1}$ and much larger than broadening coefficients for the H_2O-N_2 collisions, which are 0.1 $cm^{-1}atm^{-1}$. Average ratio of self-broadening coefficients to those by air, N_2 and O_2 are equal to 4.78, 4.3, 8.1 for the (301)–(000) band and 4.85, 4.4, 8.1 for the (221)–(000) band correspondently.

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