Pressure Broadening and Shift of Some H$_2$O Lines in the $\nu_2$ Band: Revisited


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Pressure-induced line broadening and line shift of three rovibrational transitions in the $\nu_2$ band and three in the $2\nu_2 - \nu_2$ hot band of H$_2$O at 7 $\mu$m were remeasured, using the wavelength-stabilized Cologne diode laser spectrometer with an upgraded recording system: the determination of the absolute line positions was better than 1 MHz, whereas the sensitivity and the long-term stability were improved by at least a factor of 10. The shift coefficient was found to be linearly dependent on the mixing ratio of the foreign gases oxygen and nitrogen for all transitions investigated, including the $13_{3,12} \rightarrow 14_{4,13}$ transition for which we previously reported a nonlinear behavior. This greatly improved consistency of the present experimental data sets allows a check on the applicability of various profile functions: a comparison between the Galatry and a Voigt profile function with floating Doppler width indicates that both reproduce the experimental values very well. Purely the ease of use gives the edge to the Voigt profile with floating Doppler width.

I. INTRODUCTION

Pressure effects exhibited by molecular transitions enjoy a growing interest for a variety of reasons: on purely spectroscopic grounds precisely determined molecular line parameters — such as pressure shift, pressure broadening, and line shape — reveal details of the collisional process encountered by the molecule. By fitting different model functions, such as Gaussian, Lorentz, Voigt, Galatry (1), and Rautian (2) profiles, to the experimental data, one should eventually be in a position to discriminate between the different physical processes prevailing during the collision. However, very reliable experimental data are required but are difficult to attain. Therefore, different methods of measurement are very desirable to independently secure the data and possibly locate and exclude sources of errors.

In planetary atmosphere research, such as the investigation of the Venustian and Jovian atmospheres, precise line positions are required for wind velocity determinations, whereas the shift and broadening parameters are used, e.g., for scaled height determinations.

Due to its strong absorption bands in the infrared, water vapor plays an important role in the radiative transfer properties of the Earth’s atmosphere. Therefore any calculation of the heat balance of the lower atmosphere requires precise knowledge of water vapor line parameters like intensities, broadening, and shift parameters, including their temperature dependence (3).

The early stages of the Cologne laboratory measurements of the pressure broadening and shift for several H$_2$O lines in the $\nu_2$ band by argon, oxygen, nitrogen, and air with a stabilized diode laser system were described in (4). The main results of these studies were twofold: (i) both the line shift and the line broadening are linear functions of pressure and (ii) for two transitions, the observed line shifts due to air could not be calculated as the weighted mean of the shifts measured for oxygen and nitrogen separately. With the improved accuracy and sensitivity of the present Cologne wavelength-stabilized diode laser system, it now seemed desirable to remeasure at least one of the two lines in question and extend the measurements to a few additional H$_2$O transitions. It should, however, be noted that the limitation of the achieved accuracy of the present measurements is set by the baseline effects caused by atmospheric H$_2$O.

With these improved measurements in accuracy and sensitivity, it became of interest to fit these new H$_2$O data to different profile functions. In our earlier work (4) we have found that the experimentally observed lineshapes can be fitted well with a Voigt profile with floating Doppler width. We have extended this lineshape fitting procedure in the present paper to include the Galatry function, with the result that both functions represent the experimental data equally well.

II. EXPERIMENTAL DETAILS

A general description of the wavelength-stabilized diode laser spectrometer has been presented in our previous papers (4–7). Due to the improvements both in the length of the absorption path (now 250 m) and in the speed of the scanning electronics, we have increased the accuracy and sensitivity of the spectrometer by about an order of magnitude. Now we are able to measure with great reliability line profiles in a wide pressure range.

All spectra were recorded at room temperature (24 $\pm$ 2°C). The accuracy of the frequency position measurement...
FIG. 1. Lorentz widths obtained by fitting the generalized Voigt function to synthetic Galatry profiles ($\gamma = 33$ MHz/bar, $\beta_c = 1100$ MHz/bar) modified by the addition of artificial noise. The straight line is the linear regression curve for the data above 1 bar.

FIG. 2. Gauss widths obtained by fitting the generalized Voigt function to synthetic Galatry profiles. See also the legend to Fig. 1.
to better than 1 MHz was achieved by stabilizing the diode laser on an interference maximum of an internally coupled Fabry–Perot interferometer (icFPI) of variable optical length. Improvement of the sensitivity of the spectrometer was achieved in two ways: (i) by simply increasing the path length of the Herriott cell up to 250 m and (ii) by increasing the scanning speed of the diode, which resulted in a decrease in the low-frequency laser noise. In the present study each single scan takes about 1 sec, which should be compared with 20 min per scan in our old measurement procedure. Up to 400 scans were coadded for each pressure setting. By this method the signal-to-noise ratio of the recorded spectra was improved significantly.

In order to secure the accuracy of the frequency determination of a specific H₂O transition during the pressure dependence measurements, we simultaneously monitored lines of the reference gas N₂O. The position of an H₂O line has been measured relative to a strong N₂O line. Previously the positions of an H₂O line at different pressures had been measured relative to each other. Therefore, unnoticed frequency jumps, either of the diode laser or of the He–Ne laser from one interference maximum of the icFPI to another, could not be fully ruled out and might potentially have been one cause of error apparently encountered in some of the previous shift measurements.

Another cause of error, which might have gone unnoticed and which is therefore difficult to assess, resides with the purity of the sample used. Unspecified trace constituents may falsify the measurements. Especially H₂O impurities outgassing from the walls of the cell may cause effects which cannot be quantified. In the present experiments we have used dry oxygen and nitrogen and artificial air (78% N₂, 22% O₂) in order to minimize these effects.

For the measurement of the transition 13₂,₁₂ ← 14₁,₁₃ at 1326.33158 cm⁻¹, the cell was initially filled with 2 mbar of H₂O to which either N₂ or O₂ as appropriate was added. Then the pressure was raised to about 1 bar by the appropriate foreign gas. For each mixture of foreign gas, 12 to 16 spectra were recorded at pressures between 13 and 1010 mbar. For determining the self effects 14 different spectra at pressures between 4 and 20 mbar of pure H₂O were recorded. In order to maintain a reasonable absorption strength during the self-effect measurements, the Herriott cell had to be adjusted to 60 m absorption path length. We used deuterium-depleted water for these measurements to prevent overlap of the H₂O absorption line with an HDO line which occurs just about 800 MHz away.

In addition, we have measured the pressure effects on the lines near 1316 cm⁻¹ in a similar manner; 1₁₃,₈ ← 1₂₄,₉, 1₁₂,₂ ← 1₁₅,₆, and three hot band transitions as listed in Tables 1 and 2.

III. DATA ANALYSIS

A few remarks on the details of the fitting procedure may be appropriate here, since accurate determination of both the

**FIG. 3.** An example of the observed spectrum of the 13₂,₁₂ ← 14₁,₁₃ transition compared with the best fit calculated one.
FIG. 4. The dependence of measured and fitted half-widths of the $13_{2,12} \leftrightarrow 14_{1,13}$ transition on the pressure of the foreign gas oxygen. The uncertainty increase for pressures $p > 800$ mbar is caused by the baseline difficulty.

The line shift and the line broadening is susceptible to various selection criteria of the raw data. Neglecting problems like the determination of the baseline level, the line shift can be obtained directly from the experiment. In contrast to the line shift determination, the evaluation of the collisional broadening parameter usually requires a lineshape function based on a theoretical model of the collisional process. Since the linewidth at lower pressures is dependent on competing effects, it is only at higher pressures well above the Dicke minimum that the broadening parameter can be deduced directly from the measured linewidth. At high pressures on the other hand the determination of the linewidth is often hampered by other nearby overlapping lines and the impact of baseline distortions, which are more pronounced for a heavily broadened line.

A common method in diode laser spectroscopy for securing the pressure-dependent quantities consists in the determination of the line parameters of the Voigt profile at several moderate pressures and the subsequent fit of a linear regression curve to the pressure dependence of the Lorentz width. Deviations between the measured profiles and the Voigt profile can easily be observed in the low-pressure range since the Voigt profile cannot describe any narrowing effects. This behavior is borne out in Fig. 1 where the determined Lorentz linewidths of synthetic Galatry profiles are plotted vs pressure. Figure 2 shows that, at low pressure, the Gaussian width decreases with increasing pressure. The Rautian and the Galatry profile, resulting from the hard and soft collision model, are the better choices for profile functions.

Compared to our earlier measurements the signal-to-noise ratio of the present data has been improved by at least an order of magnitude. It seems, therefore, warranted for the

<table>
<thead>
<tr>
<th>Transition</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>Air†</th>
<th>$H_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$13_{2,12} \leftrightarrow 14_{1,13}$</td>
<td>412(3)</td>
<td>262(3)</td>
<td>381(3)</td>
<td>5400(300)</td>
</tr>
<tr>
<td>$11_{2,10} \leftrightarrow 12_{1,9}$</td>
<td>1969(36)</td>
<td>785(37)</td>
<td>1904(63)</td>
<td>10600(500)</td>
</tr>
<tr>
<td>$11_{2,9} \leftrightarrow 11_{1,8}$</td>
<td>2290(200)</td>
<td>971(45)</td>
<td>2048(210)</td>
<td>8400(600)</td>
</tr>
</tbody>
</table>

Table 1

<table>
<thead>
<tr>
<th>Hot band $\nu_2 = 2 \leftrightarrow 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5_{2,4} \leftrightarrow 6_{1,3}$</td>
</tr>
<tr>
<td>$5_{4,2} \leftrightarrow 6_{2,1}$</td>
</tr>
<tr>
<td>$5_{4,1} \leftrightarrow 6_{3,2}$</td>
</tr>
</tbody>
</table>

Each number in parenthesis is one standard deviation in units of the last digit.
Numbers in italic are the values for air, calculated from the nitrogen and oxygen values.
† artificial air: 78 % $N_2$, 22 % $O_2$
TABLE 2
Shift of H2O Lines by Nitrogen, Oxygen, Air, and Water
(in MHz/bar)

<table>
<thead>
<tr>
<th>Transition</th>
<th>N2</th>
<th>O2</th>
<th>Air†</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>132,12 → 141,13</td>
<td>-111.3(13)</td>
<td>-115.4(16)</td>
<td>-114.5(26)</td>
<td>132(24)</td>
</tr>
<tr>
<td></td>
<td>-112.8(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>113,8 → 124,9</td>
<td>-351(21)</td>
<td>-180(37)</td>
<td>-327(13)</td>
<td>-625(30)</td>
</tr>
<tr>
<td></td>
<td>-313(18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>112,9 → 115,6</td>
<td>-369(62)</td>
<td>-250(11)</td>
<td>-378(41)</td>
<td>-445(30)</td>
</tr>
<tr>
<td></td>
<td>-348(48)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot band ν2 = 2 ← 1</td>
<td>52,4 ← 63,3</td>
<td>-51(51)</td>
<td>-109(9)</td>
<td>379(32)</td>
</tr>
<tr>
<td></td>
<td>-55(8)</td>
<td>-65(49)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>54,2 ← 65,1</td>
<td>17(41)</td>
<td>-86(4)</td>
<td>14(12)</td>
<td>265(25)</td>
</tr>
<tr>
<td></td>
<td>-6(98)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>58,1 ← 65,2</td>
<td>65(15)</td>
<td>-67(3)</td>
<td>66(17)</td>
<td>225(40)</td>
</tr>
<tr>
<td></td>
<td>86(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each number in parenthesis is one standard deviation in units of the last digit.

Numbers in italics are the values for air, calculated from the nitrogen and oxygen values.

† artificial air: 78 % N2, 22 % O2.

The pressure broadening and shift results obtained in the present study are listed in Tables 1 and 2, respectively. As observed previously (10–13), the H2O self-broadening effect is about one order of magnitude larger than the broadening by N2. The broadening by N2 is about twice the broadening by O2. On the other hand, the shift coefficients of N2 and O2 exhibit about comparable values, but depending on the transition they vary in sign. The self-shifts in H2O are considerably larger than the shifts by foreign gases (by about a factor of 3), but the direction of the shift seems to be uncorrelated to the O2 and N2 shifts.

It can readily be seen that the shifts for the transition 132,12 ← 141,13 due to oxygen and nitrogen gases are essentially identical, and consequently the shift due to artificial air lies in the same range. This finding is in contradiction to our earlier results (4). Presumably this originates from unnoticed frequency jumps in the laser locking procedure in our previous measurements.

The broadening of this line by artificial air coincides to within 0.5% with the value expected from the broadening coefficients of N2 and O2. The self-effect due to the finite amount of H2O in the sample gas was corrected by assuming additivity of the pressure effect parameters.

The main source of errors in the present measurements resides with the unknown background contribution. The usual approximation of the background by a quadratic polynomial (14) was insufficient for the 132,12 ← 141,13 transition since the absorption by this line due to water vapor in the optical path outside the gas cell is clearly visible. For this reason the background line caused by atmospheric H2O was fitted with a generalized Voigt function simultaneously.

A simultaneous fitting of lines resulting from absorption inside and outside the cell was not possible for the group of five lines around 1316 cm−1 because of a strong correlation between the parameters. Instead we described the background with a polynomial and limited the evaluation to lower pressures. Since the 1σ errors of the fit given in the tables refer to an evaluation with this simplifying model for the background, the slight deviation of some coefficients of air from the values obtained by a linear interpolation between the N2 and O2 coefficients should not be overrated.

V. CONCLUSION

In this paper we have clearly demonstrated that the shift coefficients due to binary mixtures of foreign gases behave...
linearly with the mixing ratio. In fact for all molecules, i.e., H₂O and NH₃, except H₂ (15), measured so far in our laboratory the shift and broadening coefficients are found to depend linearly on the mixing ratios of the foreign gases. It seems highly likely that the nonlinear line shift behavior of the 9 5, 10, transition also reported in our previous paper (4) has to be corrected in a similar fashion. In addition we have shown that the observed line profiles are equally well represented by a generalized Voigt or a Galatry function.

**APPENDIX**

The transmission of the laser radiation through a cell with gas is given by

\[ I(\nu) = I_0(\nu) \exp(-\kappa(\nu)), \]

where \( \kappa \) is the dimensionless absorbance. To the measured signal \( I(\nu) \) we fit a function of the form

\[ (c_0 + c_1 \nu + c_2 \nu^2) \exp(-Sf(\nu - \nu_0)). \]

The quadratic polynomial approximates the intensity of the incident radiation which includes the effect of atmospheric absorption, \( S \) is the integrated line intensity, and \( f(\nu - \nu_0) \) represents the line profile function for a single line centered at \( \nu_0 \). The Voigt profile function is given by (16)

\[ V(x', y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{e^{-i} \exp(-ix't - yt)}{(x' - t)^2 + y^2} dt \]

with

\[ x' = (\nu - \nu_0 - \delta p)/\gamma_d' \quad \text{and} \quad y = \gamma_l/\gamma_d' = \gamma p/\gamma_d', \]

where \( \nu_0 \) is now the frequency of the center of the unshifted line. \( \gamma_l \) is the Lorentz width (HWHM), \( \delta \) is the pressure shift and \( \gamma \) the pressure broadening coefficient, and \( p \) is the pressure. \( \gamma_d' \) is the theoretical 1/e Doppler half-width given by the frequency of the transition, the mass of the radiating molecule, and the temperature of the gas.

The same profile function is used for the generalized Voigt profile. However, in contrast to the usual Voigt profile, the Doppler width is no longer fixed to the theoretical value, but it is treated as a free parameter of the fit. This allows an empirical consideration of the Dicke narrowing effects. Since the frequency scale \( (x') \) is given in units of the Doppler width, we actually use the function \( f(\nu - \nu_0) = (\sqrt{\pi} \gamma_d')^{-1} V(x', y) \) for the Voigt profile normalized to 1. It is obtained by convoluting a Lorentz profile with a Gauss profile. The numerical evaluation of the profiles is done with the algorithms and approximants given by Hui et al. (17), Herbert (18), and Varghese and Hanson (16).

The Galatry profile function is given by (16)

\[ G(x', y, z) = \frac{1}{\sqrt{\pi}} \text{Re} \left( \int_{0}^{\infty} \exp \left( -ix't - yt \right) \right. \]

\[ + \frac{1}{2z^2} (1 - zt - \exp(-zt)) dt \],

where

\[ z = \beta_0 p/\gamma_d' \]

is the standardized contraction parameter, where \( \beta_0 \) is the contraction coefficient in units of frequency per pressure, and \( x' \) and \( y \) are as given above. In the limit \( z \to 0 \) this profile becomes identical to the ordinary Voigt profile. The Rautian profile is numerically quite similar to the Galatry profile, although the two profiles are derived from different assumptions about the effect of collisions on the change of the velocity of the radiating molecules (2). At the present time a direct distinction between the two profiles is not possible with our spectrometer.

As a result of the experiments we wanted to determine accurate values of the broadening, \( \gamma \), and contraction, \( \beta_0 \), coefficients. For testing the most adequate procedure, a number of synthetic spectra were computed for different pressures using Galatry profiles. The experimental conditions were simulated by adding artificial noise to the calculated spectra. Finally, fits to these spectra were calculated using Galatry or generalized Voigt profiles. As it turned out fits with Galatry profiles converged rather poorly, and large uncertainties of the contraction parameter were found. This is due to the strong correlation of the contraction and broadening parameters, from which it became immediately clear that it is impossible to derive reliable broadening and shift coefficients from a line profile measured at one pressure.

Using the generalized Voigt profile the fits converged very well and the fit parameters were found with very little uncertainty. In addition the residuals observed — calculated generally were smaller than the noise of the data. The Lorentzian width obtained as a function of pressure might serve as the data basis for the determination of the pressure broadening coefficient, but in the presence of Dicke narrowing the result is misleading. As shown in Fig. 1, the Lorentz width obtained from the generalized Voigt profile depends in the Dicke narrowing region nonlinearly on the pressure, and the slope of the best fit line to these data underestimates the value for the broadening coefficient. Moreover the regression line has a nonzero value at zero pressure. As mentioned in the text, one could determine the broadening coefficient better by using only the data at high pressures well above the Dicke minimum, but the uncertainty about the background and the impact of neighboring lines interfere. Our simulations showed that the slope of the linear regres-
The dependence of the half-width obtained from the fit of synthesized spectra (dots) on pressure is fitted to the Galatry function (solid line).

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REFERENCES
