



LASER PHOTOACOUSTIC SPECTROSCOPY IN SUPERSATURATED WATER VAPOR

J. Hinderling, M. Sigrist, F. Kneubühl

► To cite this version:

J. Hinderling, M. Sigrist, F. Kneubühl. LASER PHOTOACOUSTIC SPECTROSCOPY IN SUPERSATURATED WATER VAPOR. Journal de Physique Colloques, 1983, 44 (C6), pp.C6-559-C6-564. 10.1051/jphyscol:1983692 . jpa-00223251

HAL Id: jpa-00223251

<https://hal.science/jpa-00223251>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LASER PHOTOACOUSTIC SPECTROSCOPY IN SUPERSATURATED WATER VAPOR

J. Hinderling, M.W. Sigrist and F.K. Kneubühl

Physics Department, ETH, CH-8093 Zurich, Switzerland

Résumé - L'explication du continu d'absorption dû à la vapeur d'eau dans la fenêtre atmosphérique entre 8 μm et 14 μm étant controversée, des mesures précises de l'absorption à haute humidité relative sont d'un grand intérêt. Nous présentons les premières mesures photoacoustiques faites dans de la vapeur d'eau sursaturée dans une chambre de diffusion. Le rôle joué par les multimères d' H_2O et les conséquences de nos résultats pour l'interprétation de la transmission de l'atmosphère sont discutés.

Abstract - Since the primary cause of the water vapor continuum absorption within the 8-14 μm atmospheric window is controversial, accurate absorption measurements at high relative humidity are of great interest. We present the first photoacoustic studies performed in supersaturated water vapor in a diffusion chamber. New results on the role of water clusters with respect to the atmospheric transmission are discussed.

I - INTRODUCTION

The transmission of the atmospheric window in the spectral region between 8-14 μm is limited by a weak continuum absorption which is mainly due to water vapor. Although numerous studies on the mechanisms of this ir continuum water vapor absorption have been performed it is still not well understood. Several explanations are suggested:

- a) extreme-wing absorption from strong lines of the H_2O monomers /1/,
- b) ir absorption by stable dimers consisting of two water molecules in thermodynamic equilibrium /2/,
- c) absorption by larger molecular complexes of water such as ionic clusters /3/, non-equilibrium clusters /4/ or hydrated aerosols.

Simple line shape theories like local Lorentzian line calculations do not predict correctly the characteristics of the continuum absorption of the lower atmosphere particularly regarding the steep negative temperature dependence. Improved line shape theories yield a considerably better but not yet satisfactory agreement with measured absorption data /5/.

Varanasi et al /6/ were the first to suggest that dimers might be responsible for the strong temperature dependence of the continuum. The dimer population decreases rapidly with increasing temperature, thus the absorption due to dimers exhibits a negative temperature dependence. Dimer calculations by Suck et al. /7/ yield for the strongest of the six intermolecular motions a frequency of 624 cm^{-1} close to the atmospheric window considered. Although the fractional concentration of dimers is small ($\approx 4 \cdot 10^{-4}$) compared to the concentration of H_2O -monomers, it is argued that the absorption would still be large enough to be detected in this transmittance window. The calculated dimer absorption coefficient /7/ varies from 10^{-22} to $10^{-21} \text{ cm}^2 \text{ mol}^{-1} \text{ atm}^{-1}$ within 8 μm to 16 μm at a dimer concentration of $7.6 \cdot 10^{14} \text{ cm}^{-3}$ at 14 torr water vapor pressure and 296 K. This result is in qualitative agreement with

experimental data by Burch et al./1/. It appears that stable water dimers are an important mechanism for the continuum absorption even at low partial pressures.

The controversial role of larger water clusters has been discussed extensively in the literature /8/.

In conclusion, present theoretical and experimental studies cannot decide conclusively on the real cause of the observed continuum absorption. Our new experimental data should be well suited to give a new impetus to this matter because they represent the first results obtained in supersaturated water vapor, i.e. at increased cluster concentrations.

II - EXPERIMENTS

a) Laser Photoacoustics

Since the absorption coefficient of water vapor at $10\text{ }\mu\text{m}$ is typically only 10^{-6} cm^{-1} at a partial pressure of 10 mbar, we use laser photoacoustic spectroscopy for absorption studies. Its high sensitivity permits reliable measurements in small gas cells. Consequently homogeneous water vapor concentrations are realized in contrast to field experiments and long path measurements either in tubes or in large multipath cells /9/. In addition, critical parameters like sample pressure, total pressure, temperature etc. can easily be controlled.

b) Experimental Setup

Our experimental arrangement is typical for photoacoustic studies in gases. We use a grating-tuned cw CO_2 laser which emits on nearly 70 transitions between $9.3\text{ }\mu\text{m}$ and $10.8\text{ }\mu\text{m}$. The laser beam passes through a sealed gas cell of special design described previously /10/. This spectrophone cell is constructed similar to an upward thermal diffusion chamber /11/, thus allowing measurements in supersaturated water vapor. The responsivity of the cell with a volume of 200 cm^3 and an absorption length of 14 cm is enhanced by an acoustic resonance at ca. 1.9 kHz. The incident laser beam is modulated with a chopper. The periodically generated acoustic signals in the cell are monitored with a miniature electret microphone and fed into a lock-in amplifier using the chopper frequency as reference. Behind the spectrophone cell a bolometer detects the laser power for normalization.

Absolute absorption coefficients are obtained by calibrating the system with known amounts of ethylene using the absorption coefficients at different CO_2 laser transitions given in Ref. 12. Commercial gas mixtures of 10 ppm ethylene in argon or 15 ppm ethylene in nitrogen were used. Taking the CO_2 laser transitions P(24) and P(28) within the $10.4\text{ }\mu\text{m}$ band, we achieved an average minimum detectable concentration of 15 ppb for ethylene corresponding to an absorption coefficient of ca. $4 \cdot 10^{-7}\text{ cm}^{-1}$. Therefore our apparatus is suited for absorption measurements at H_2O pressures as low as 5 mbar.

III - MEASUREMENTS, RESULTS AND DISCUSSION

a) Below Saturation

The weak water vapor absorption in the $8\text{--}14\text{ }\mu\text{m}$ atmospheric window is dominated by a continuum absorption in addition to a number of absorption lines /13/. However, these lines, e.g. at the R(20) $10.25\text{ }\mu\text{m}$ transition, are very weak compared to the H_2O ir transitions at 1600 cm^{-1} . Accurate absorption measurements in this wavelength region at different water-vapor partial pressures, temperatures and wavelengths are required for testing existing theoretical models. Our first experiments were devoted to the pressure dependence. These measurements were performed in the diffusion chamber operated below saturation

in thermal equilibrium at room temperature. Argon was used as carrier gas at a total pressure of 950 mbar. In Fig. 1 the pressure dependence of the continuum absorption at the P(20) 10.59 μm laser transition is compared to that of the line absorption at the R(20) 10.25 μm transition.

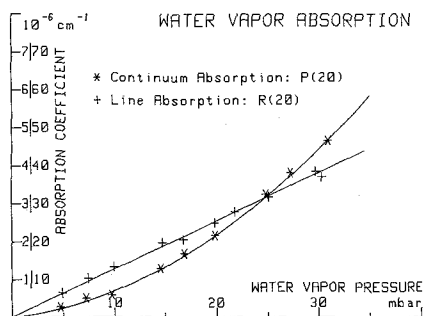


Fig. 1 - Dependence on the water-vapor partial pressure of both the continuum absorption at 10.59 μm and the line absorption at 10.25 μm .

Since water vapor has an absorption line centered at 10.246 μm /14/, i.e. very close to the R(20) 10.247 μm laser transition, the linear pressure dependence observed in our measurements is in excellent agreement with theoretical considerations. In contrast to the line absorption, the pressure dependence of the continuum absorption at the P(20) 10.59 μm transition is quadratic. This behaviour cannot be explained with monomeric line-center absorption, but agrees with predictions from both extreme-wing calculations and dimer models /15/.

For a mixture of H_2O and a foreign gas the H_2O continuum extinction coefficient α is often written in terms of line broadening contributions /15/

$$\alpha(p_w) = C_s^0 \cdot n_w \cdot \{p_w + \gamma(p_t - p_w)\} \quad \text{with} \quad \gamma = C_f^0/C_s^0$$

where $C_s^0(\lambda, T)$ and $C_f^0(\lambda, T)$ are the continuum coefficients for self broadening and foreign broadening, respectively. The water-vapor partial pressure is represented by p_w , the total pressure by p_t . n_w denotes the number of water molecules (monomers) per cm^3 . A regression fit of our measurements yields the values

$$C_s^0 = 1.61 \cdot 10^{-22} \text{ cm}^2 \text{ mol}^{-1} \cdot \text{atm}^{-1}$$

$$\gamma = 0.0085$$

in fair agreement with literature. Shumate et al. /16/ obtained $C_s^0 = 1.46 \cdot 10^{-22} \text{ cm}^2 \text{ mol}^{-1} \text{ atm}^{-1}$ and $\gamma = 0.011$ also from spectrophone measurements whereas McCoy et al. /9/ reported on long-path measurements which yielded $C_s^0 = 1.96 \cdot 10^{-22} \text{ cm}^2 \text{ mol}^{-1} \text{ atm}^{-1}$ and $\gamma = 0.005$. Line-shape calculations by Nordstrom et al. /5/ give $C_s^0 \approx 2 \cdot 10^{-22} \text{ cm}^2 \text{ mol}^{-1} \text{ atm}^{-1}$ at room temperature. It has to be pointed out that the small ratio γ between the foreign and the self broadening coefficient is affected with a large error because C_f^0 for nitrogen or air is too small to be measured accurately. Comparing our value of γ with literature it has to be reminded that our γ was obtained for a water vapor-argon mixture in contrast to measurements cited in literature which were performed with nitrogen or air as foreign gas.

b) Supersaturation

Since the water-cluster concentration increases with relative humidity /17/, absorption measurements in supersaturated water vapor are of great interest. Studies of this type can reveal information on the contribution of dimers and larger clusters to the continuum absorption. Experiments at different supersaturation ratios, thus at different dimer or cluster concentrations, can be performed in our diffusion chamber simply by varying the vertical position of the laser beam between the heated bottom and the cooled top plate. Fig. 2 shows a plot of the measured continuum absorption in supersaturated water vapor as a function of the vertical position x of the laser beam within the chamber. The temperature of the liquid pool at the bottom was kept at 327 K that of the top plate at 294 K. The total pressure in the cell was 950 mbar with nitrogen as carrier gas.

HEIGHT VARIATION OF IR ABSORPTION

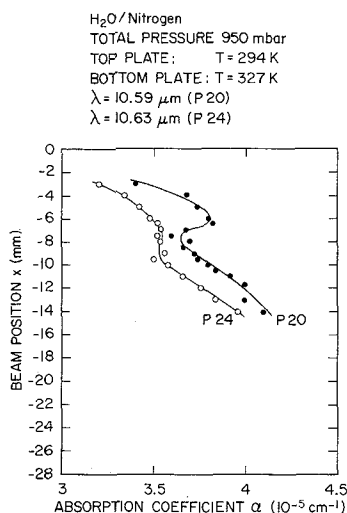


Fig. 2 - Measured height profiles of the continuum absorption in supersaturated water vapor at the P(20) $10.59 \mu\text{m}$ and P(24) $10.63 \mu\text{m}$ laser transitions. Top plate at $x = 0 \text{ mm}$, bottom plate at $x = -28 \text{ mm}$.

Both height profiles show a characteristic maximum of the continuum absorption close to the top plate ($x \approx -7 \text{ mm}$). This behaviour has also been found at other laser transitions within the continuum as well as for other carrier gases. This interesting result may be interpreted as superposition of the following effects:

- i) Since both the partial pressure of the water vapor and the temperature increase almost proportional to the vertical position x /18/, a general increase of the continuum absorption is expected. However, it has to be less than the quadratic increase with partial pressure shown in Fig. 1 due to the simultaneous temperature increase.
- ii) The supersaturation ratio S and thus also the cluster concentration exhibits a maximum with respect to the position x close to the top plate /19/.

Consequently, the observed relative absorption maximum at $x \approx -7 \text{ mm}$ could be due to the enhanced water-cluster concentration around this position.

In contrast to the continuum absorption, the H_2O line absorption shows an entirely different height profile under identical conditions. Fig. 3 represents the measured line absorption taken at the laser transition R(20) $10.25 \mu m$ which is about four times higher than the continuum absorption shown in Fig. 2.

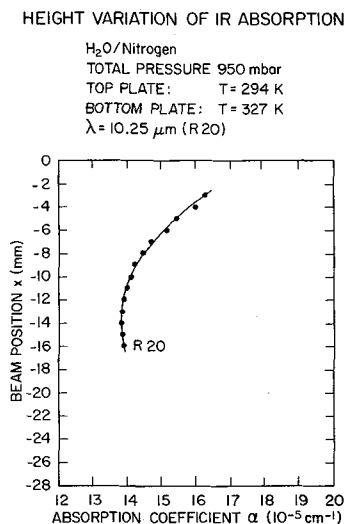


Fig. 3 - Measured height profile of the line absorption in supersaturated water vapor at the R(20) $10.25 \mu m$ laser transition. Top plate at $x = 0$ mm, bottom plate at $x = -28$ mm.

Since the continuum absorption does not vary strongly with wavelength $1/\lambda$, the underlying continuum in Fig. 3 is at the most one quarter of the total absorption at the R(20) transition. Consequently the measured data in Fig. 3 are mainly due to water monomer absorption although the corresponding partial pressure reaches up to 88 mbar in the mid plane of the chamber. A significant deviation in the height profile which could be attributed to existing clusters cannot be observed. The measured profile can be explained on the basis of the water monomer line-center absorption taking its pressure and temperature dependence into account.

IV - CONCLUDING REMARKS

Hitherto, the real mechanism of the water vapor continuum absorption within the $8-14 \mu m$ atmospheric window is not well understood. In general three different causes are considered, namely extreme-wing absorption by water monomers, absorption by water dimers and by more complex water clusters. Absorption measurements at constant temperature for low water vapor pressures $p_w \leq 30$ mbar show both the expected linear pressure dependence for water monomer line-center absorption and the expected quadratic pressure dependence for the continuum absorption. However these experimental data are not suited to form a decisive opinion about the theoretical models. With regard to a possible contribution of water dimers or clusters to the continuum absorption we performed first absorption measurements in supersaturated water vapor. These experiments were carried out with a photoacoustic cell constructed as an upward thermal diffusion chamber. A drastic difference between line and continuum absorption with respect to the supersaturation ratio has been obtained. These results indicate that at least for high relative humidity water clusters have to be taken into account for the interpretation of the ir continuum absorption. However, more experimental data including the temperature dependence of the absorption are required before quantitative predictions on the infrared activity of water clusters can be made.

ACKNOWLEDGMENTS

This work was supported by the GRD of EMD and by the ETH Zurich.

REFERENCES

- / 1/ BURCH D.E. and GRYVNACK D.A., "Atmospheric Water Vapor", DEEPAK A., WILKERSON T.D. and RUHNKE L.H., Eds., Academic Press, New York, 1980, p 47.
- / 2/ WOLYNES P.G. and ROBERTS R.E., Appl. Opt. 17 (1978) 1484.
- / 3/ CARLON H.R., Infrared Physics 22 (1982) 43.
- / 4/ ZAVODY A.M., EMERY R.J., GEBBIE H.A., Nature 277 (1979) 462.
- / 5/ NORDSTROM R.J. and THOMAS M.E., "Atmospheric Water Vapor", DEEPAK A., WILKERSON T.D. and RUHNKE L.H., Eds., Academic Press, New York, 1980, p. 77.
- / 6/ VARANASI P., CHOU S. and PENNER S.S., J. Quant. Spectrosc. Radiat. Transfer 8 (1968) 1537.
- / 7/ SUCK S.H., WETMORE A.E., CHEN T.S. and KASSNER J.L., Jr., Appl. Opt. 21 (1982) 1610.
- / 8/ CARLON H.R., Infrared Phys. 19 (1979) 49.
- / 9/ MCCOY J.H., RENSH D.B and LONG R.K., Appl. Opt. 8 (1969) 1471.
- /10/ HINDERLING J., SIGRIST M.W., and KNEUBUEHL F.K., Proc. Lasers'82, New Orleans, STS press, 1982, to be published.
- /11/ KATZ, J.L. and OSTERMIER B.J., J. Chem. Phys. 47 (1967) 478.
- /12/ KONJEVIC N. and JOVICEVIC S., Spect. Lett. 12 (1979) 259.
- /13/ HINDERLING J. and SIGRIST M.W., Helv. Phys. Acta 54 (1981) 637.
- /14/ HORTON R.F., Proc. SPIE 195, Atmospheric Effects on Radiative Transfer, 1979, p. 46.
- /15/ ROBERTS R.E., SELBY J.E.A. and BIBERMAN L.M., Appl. Opt. 15 (1976) 2085.
- /16/ SHUMATE M.S., MENZIES R.T., MARGOLIS J.S. and ROSENGREN L.-G., Appl. Opt. 15 (1976) 2480.
- /17/ KATZ J.L., MIRABEL P., SCOPPA C.J. II and VIRKLER T.L., J. Chem. Phys. 65 (1976) 382.
- /18/ FRANCK J.P. and HERTZ H.G., Z. Phys. 143 (1956) 559.
- /19/ KATZ J.L., J. Chem. Phys. 52 (1970) 4733.