Investigation of interaction of carbon dioxide with aerogel's nanopores

A.A. Solodov[1,2], T.M. Petrova[1], Yu.N. Ponomarev[1,2], A.M. Solodov[1],
I.A. Vasilenko[1], V.M. Deichuli[2]

[1]V.E. Zuev Institute of Atmospheric and Oceanic Optics, SB RAS, Tomsk, 634055, Russia
[2]National Research Tomsk State University, Lenina av. 36, Tomsk 634050, Russia

ABSTRACT

The absorption spectrum of 2 0 0 12 – 0 0 0 01 band of carbon dioxide, confined in 20 nm nanopores of silica aerogel, was measured with help of a Bruker IFS 125 HR Fourier transform spectrometer at room temperature and a spectral resolution of 0.01 cm^{-1}. The obtained dependence of spectral line half-width values on rotational quantum numbers was studied and compared with data available in the literature.

Nanoconfinement, Fourier transform spectroscopy, CO_2, spectral line broadening

1. Introduction

In recent years, the investigation of absorption spectra of gases confined in nanoporous materials attracts the increasing attention of researches [1-8]. The character of interaction of molecules with the inner surface of such structures can be studied by the IR spectroscopy methods. Molecules of the studied matters can be found in gas phase in nanopores and adsorbed on their inner surface [1-4].

Studies of gas-phase molecules confined in nanopore volume started comparatively not long ago, but this topic is of great interest from the fundamental as well as applied point of view. Contrary to adsorbed molecules, which rotational freedoms are limited by surface [9], the gas phase ones have a fine rotational structure. At a low gas pressure, when intermolecular collisions are negligible, the absorption spectra are formed under strong limitation of mean free path and the line shapes and shift are predominantly determined by the collision of molecules with the nanopores walls rather than with each other. The increased collision frequency due to limitation of mean free path inside nanopores leads to the broadening of spectral lines [1-8].

The dependence of spectral line half-width values of confined molecules on rotational quantum numbers is poorly studied. In [3, 6] a very weak dependence was observed, which allowed authors to conclude that each collision with a wall, independently on rotational state, causes interruption of the process of radiation absorption [7].

Our previous measurements of absorption spectra of different gases, confined in aerogel [10] with smaller pore sizes of have shown the relatively strong dependence of spectral line widths on quantum numbers [1, 2]. In this work we performed new research on the rotational dependence of line half-widths of 2 0 0 12 – 0 0 0 01 band for confined CO_2 carried out with better signal to noise ratio.

2. Experimental details

Measurements of CO_2 absorption spectra in volume of aerogel nanopores were performed with help of Fourier transform spectrometer Bruker IFS 125 HR in the region 4800 – 5100 cm^{-1} at room temperature and at the spectral resolution of 0.01 cm^{-1}. This measurement range was chosen because of very weak self-absorption of aerogel and the

21st International Symposium on Atmospheric and Ocean Optics: Atmospheric Physics,
edited by G. G. Matvienko, O. A. Romanovskii, Proc. of SPIE Vol. 9680, 96800D
© 2015 SPIE · CCC code: 0277-786X/15/$18 · doi: 10.1117/12.2205561

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/20/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

presence of rather strong 2 0 0 12 – 0 0 0 01 absorption band of carbon dioxide [11]. The spectrometer was equipped with tungsten light source, CaF_2 beamsplitter and InSb detector cooled by liquid nitrogen. The aerogel sample was made at G.K. Boreskov Institute of Catalysis. The sample length was 55 mm, a density of 0.245 g/cm^3, the surface area and the pore sizes, determined by the method of nitrogen low-temperature adsorption [12], were 740 m^2/g and 20 nm, respectively [1].

Before the measurements the aerogel sample was put into the vacuum cell of 65 mm length, and was pumped out during 6 hours with forevacuum pump. The absorption spectrum of the pumped out sample was recorded and was used as the baseline. The measurements were performed at pressure of 95 mbar. In order to increase the signal-to-noise ratio the coaddition of 2000 interferograms was done and the filter was used.

The recorded absorption spectrum is shown in the Fig. 1. One can see that it consist of a fine structure of vibration-rotation transitions of gas-phase CO_2, located on a broad profile, corresponding to the absorption of CO_2, adsorbed on the inner surface of nanopores.

The length of the cell used in experiment was larger than the length of aerogel sample, therefore, the contribution of the gas located in gaps between cell windows and the sample should be taken into account. Fig. 2 shows that lines corresponding to the gas phase consist of two profiles, narrow one (2), corresponding to the gas located between aerogel sample and cell windows, and a wider one (1) corresponding to the CO_2 absorption in nanopores. The processing of spectral lines was performed by simultaneous fitting of Voigt and Lorentz profiles to the experimentally recorded ones (Fig. 2). To decrease the uncertainty in fitted parameters we chose isolated lines of P branch, which overlapping with ones of other absorption bands is not sufficient. The lines of R-branch were not processed because the distances between their centers are smaller as compared with P-branch.

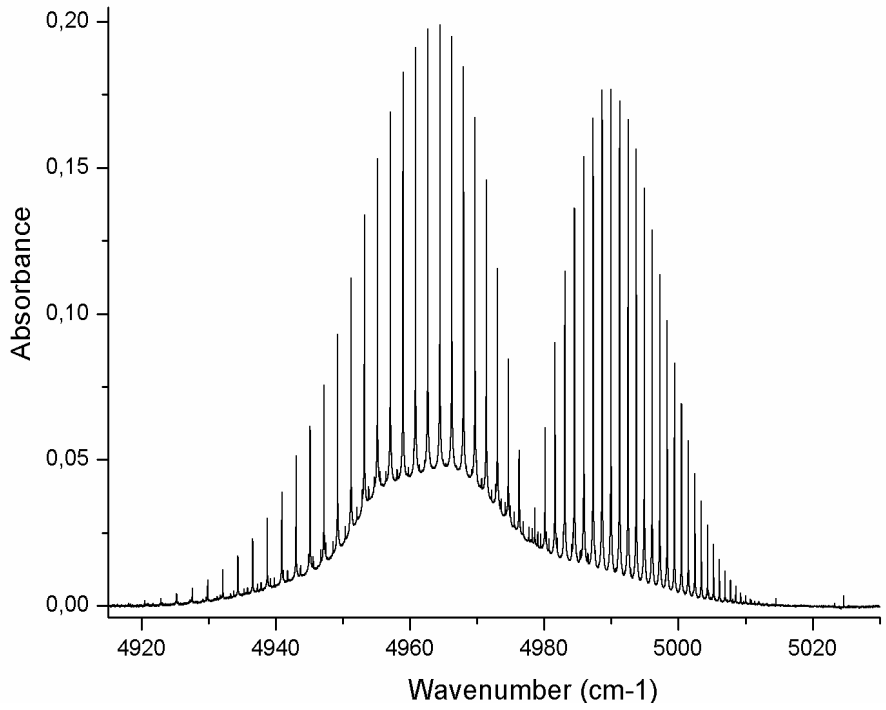

Fig. 1. Recorded spectrum formed by absorption of CO_2 molecules, adsorbed on the surface of aerogel nanopores (broad profile), and gas-phase CO_2 molecules (finely structured vibration-rotation transitions).

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/20/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

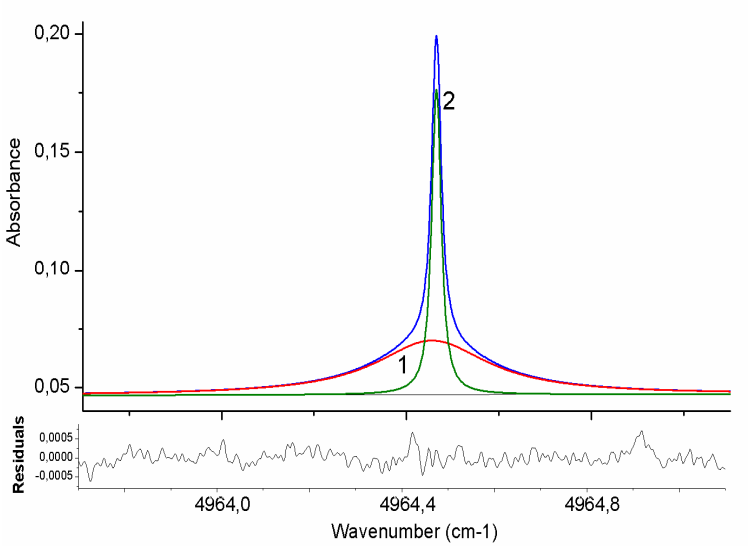

Fig. 2. Processing of carbon oxide P(16) spectral line by simultaneous fitting of Lorentz (1) and Voigt (2) profiles to experimentally recorded ones. The lower panel shows the respective residuals.

3. Results and discussion

The profile of absorption lines of molecules, located inside nanopoures, is formed due to collisions of molecules with the surface of nanostructured material (Γ_{wall}) and molecules with each other in the volume of nanopores (Γ_{mol}). According to [5,9] the contributions of Γ_{wall} and Γ_{mol} to full HWHM are additive. Γ_{wall} values were obtained by subtracting corresponding Γ_{mol} ones from full HWHM. The obtained dependence of spectral line half-width values on the rotational quantum numbers is shown on Fig. 3. In order to compare this dependence with that for free gas, the Lorenzian half-width values for free CO_2 were also plotted. For the comparison convenience set of values for free gas was multiplied by factor 12. Fig. 3 shows that half-widths values of confined CO_2 depend on rotational quantum numbers very weakly, similar dependence was observed in [3, 6] for gases confined in nanomaterials with larger pore sizes. Contrary to the results found in [3] the line shift of confined CO_2 relative to the free gas was found, its value for all lines about -0.009 cm-1.

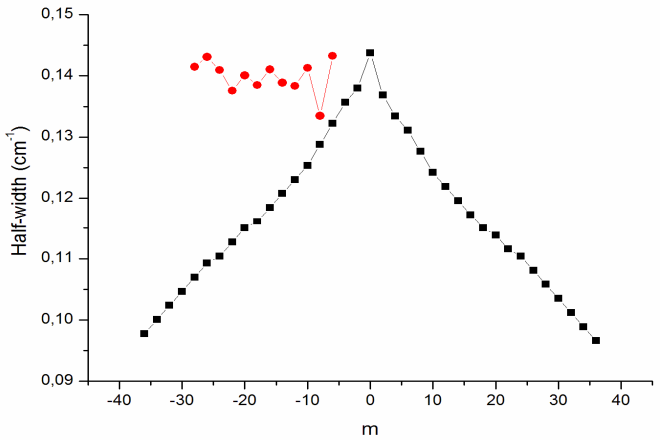

Fig. 3. Comparison of dependencies of HWHM values on rotational quantum numbers for CO2 confined in nanoporous aerogel (circles) and for the free gas (squares). For comparison convenience the set of half-width values of free CO_2 was multiplied by factor 12 (m=J for R branch and m=-J for P branch of the CO_2 absorption band).

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/20/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx

4. Conclusion

Rotational dependence of half-width values for 2 0 0 12 – 0 0 0 01 band of carbon dioxide, confined in 20 nm nanopores of silica aerogel have been studied. Contrary to the water vapor [2], the half-width values of confined CO_2 depend on moderate (from 6 to 28) rotational quantum numbers very weakly. The rotational dependence is similar with one observed in [3] for CO_2 confined in xerogel with larger pore sizes.

Acknowledgments

The authors are grateful to A. F. Daniluk for providing us the silica aerogel sample. This work was supported by the Grant of President for young scientists MK-7801.2015.2.

References

[1] Petrova, T. M., Ponomarev, Yu. N., Solodov, A. A., Solodov, A. M. and Danilyuk, A. F., "Spectroscopic Nanoporometry of Aerogel," JETP Letters. 101 (1), 65–67 (2015).

[2] Ponomarev, Yu. N., Petrova, T. M., Solodov, A. M. and Solodov A. A., "IR spectroscopy of water vapor confined in nanoporous silica aerogel," Opt. Express 18 (25), 26062 – 26067 (2010).

[3] Vander Auwera, J, Ngo, N. H., Hamzaoui, H. El, Capoen, B., Bouazaoui, M., Ausset, P., Boulet, C. and Hartmann, J.-M., "Infrared absorption by molecular gases as a probe of nanoporous silica xerogel and molecule-surface collisions: Low-pressure results," Phys. Rev. A 88, 042506 (2013).

[4] Sinitsa, L., Lavrentieva, N. and Lugovskoi, A., "Dynamic registration of D_2O absorption spectrum in silica aerogel," Mol. Phys. 112 (18), 2468–2475 (2014).

[5] Svensson, T., Adolfsson, E., Burresi, M., Savo, R., Xu, C. T., Wiersma, D. S. and Svanberg, S. "Pore size assessment based on wall collision broadening of spectral lines of confined gas: experiments on strongly scattering nanoporous ceramics with fine-tuned pore sizes," Appl. Phys. B. 110 (2), 147-154 (2013).

[6]Hartmann, J.-M., Boulet, C., Auwera, J., Hamzaoui, H. El., Capoen, B. and Bouazaoui, M., "Line broadening of confined CO gas: From molecule-wall to molecule-molecule collisions with pressure," J. Chem. Phys. 140, 064302 (2014).

[7] Hartmann, J.-M., Sironneau, V., Boulet, C., Svensson, T., Hodges, J. T. and Xu, C. T., "Collisional broadening and spectral shapes of absorption lines of free and nanopore-confined O_2 gas," Phys. Rev. A 87, 032510 (2013).

[8] Svensson, T., Lewander, M. and Svanberg, S., "Laser absorption spectroscopy of water vapor confined in nanoporous alumina: wall collision line broadening and gas diffusion dynamics," Opt. Express 18 (16), 16460–16473 (2010).

[9] Little, L. H., [Infrared spectra of adsorbed species], Academic Press (1966).

[10] Kharzheev, Yu. N., "Use of Silica Aerogels in Cherenkov Counters," Phys. Part. Nucl. 39, 107–135 (2008).

[11] Rothman, L. S., Gordon, I. E., Babikov, Y., Barbe, A., Chris Benner, D., Bernath, P. F., Birk M., Bizzocchi, L., Boudon, V., Brown, L.R., Campargue, A., Chance, K., Cohen, E.A., Coudert, L.H., Devi, V. M., Drouin, B. J., Fayt, A., Flaud, J.-M., Gamache, R. R., Harrison, J. J., Hartmann, J.-M., Hill, C., Hodges, J. T., Jacquemart, D., Jolly, A., Lamouroux, J., Le Roy, R. J., Li, G., Long, D.A., Lyulin, O. M., Mackie, C.J., Massie, S.T., Mikhailenko, S., Müller, H. S. P., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E.R., Richard, C., Smith, M. A. H., Starikova, E., Sung, K., Tashkun, S., Tennyson, J., Toon, G.C., Tyuterev, Vl. G. and Wagner, G. "The HITRAN2012 molecular spectroscopic database," JQSRT 130, 4‑50 (2013).

[12] Gregg, S. and Sing, K., [Adsorption, Surface Area and Porosity], Academic Press (1982).

Downloaded From: http://proceedings.spiedigitallibrary.org/ on 11/20/2015 Terms of Use: http://spiedigitallibrary.org/ss/TermsOfUse.aspx