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Published in:
Physical Review A (Atomic, Molecular and Optical Physics)

DOI:
[10.1103/PhysRevA.84.042705](https://doi.org/10.1103/PhysRevA.84.042705)

2011

[Link to publication](#)

Citation for published version (APA):

Xu, C., Lewander, M., Andersson-Engels, S., Adolfsson, E., Svensson, T., & Svanberg, S. (2011). Wall-collision line broadening of molecular oxygen within nanoporous materials. *Physical Review A (Atomic, Molecular and Optical Physics)*, 84(4). <https://doi.org/10.1103/PhysRevA.84.042705>

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6

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Wall-collision line broadening of molecular oxygen within nanoporous materials

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(Received 28 June 2011; published 10 October 2011)

Wall-collision broadening of near-infrared absorption lines of molecular oxygen confined in nanoporous zirconia is studied by employing high-resolution diode-laser spectroscopy. The broadening is studied for pores of different sizes under a range of pressures, providing new insights on how wall collisions and intermolecular collisions influence the total spectroscopic line profile. The pressure series show that wall-collision broadening is relatively more prominent under reduced pressures, enabling sensitive means to probe pore sizes of porous materials. In addition, we show that the total wall-collision-broadened profile strongly deviates from a Voigt profile and that wall-collision broadening exhibits an additive-like behavior to the pressure and Doppler broadening.

DOI: [10.1103/PhysRevA.84.042705](https://doi.org/10.1103/PhysRevA.84.042705)

PACS number(s): 34.10.+x, 33.70.Jg

I. INTRODUCTION

Nanoporous materials have received great attention in recent years. Such materials have, for example, been used to investigate Anderson localization of light [1], line profiles of nano-confined positronium atom emission [2], random lasing [3], storage of hydrogen and carbon dioxide [4], and efficiency enhancements of solar cells [5,6]. However, determining the internal geometrical features, such as porosity and pore sizes, remains nontrivial. One of the standard methods to assess the porosity and the pore-size distribution is mercury intrusion porosimetry [7]. The method presupposes a structure of perfect cylindrical pores that are filled with mercury under pressure and has been proven to provide incorrect results for certain porous materials [8,9]. Other methods used to assess the fine geometrical features of nanoporous materials include scanning electron microscopy (SEM) [9], x-ray computed tomography [10], radiation scattering [7], and gas adsorption techniques [7]. However, these methods are of high complexity, require long data collection times, and can be destructive or hazardous.

The use of high-resolution laser spectroscopy has been proposed as a fast and nonintrusive alternative method for pore-size assessment [11–13]. This spectroscopic method employs the fact that the size of the pores within a porous material can affect the spectroscopic line shape of a gas due to wall collisions. However, detailed descriptions on how wall collisions in porous media alter the spectroscopic line shape do not yet exist. To be able to accurately determine the internal geometrical features, deeper understanding of the influence of the pore size and geometry on the spectroscopic line shape within nanopores is certainly needed.

In this study, we present the broadening of absorption lines of oxygen (O_2) confined within two nanoporous zirconia (ZrO_2) samples having different pore sizes and investigated in a pressure range of 50 to 760 Torr. We demonstrate that the effect of wall-collision broadening is relatively more prominent under reduced pressures, enabling the possibility of assessing the pore sizes with high precision. In addition, we illustrate how the pressure series can be used to increase our

understanding of wall-collision processes and their effect on spectroscopic line shapes.

II. EXPERIMENT

The spectroscopic system used in this study is based on high-resolution tunable diode-laser absorption spectroscopy and utilizes the gas in scattering media absorption spectroscopy (GASMAS) method for detection of gases inside porous materials [11,14]. The system used is described in detail in Ref. [15] and is based on a single-mode, vertical-cavity, surface-emitting laser diode, with an output power of $P = 0.3$ mW. The laser was tuned to the R9Q10 absorption line of O_2 at 760.654 nm and was then scanned over a frequency range of 40 GHz around the absorption line. Optical interferences were suppressed by means of beam dithering [16]. For free gas under ambient conditions (at pressure $p = 760$ Torr and temperature $T = 296$ K), the R9Q10 line gives rise to a peak absorption of $2.7 \times 10^{-4} \text{ cm}^{-1}$ and a half width at half maximum (HWHM) of $\Gamma = 1.56$ GHz [17]. The nanoporous samples were made by sintering two different zirconia powders, resulting in 7-mm-thick strongly scattering pillbox shaped samples with different pore sizes (details available in Ref. [13]). The pore sizes were determined using mercury intrusion porosimetry. The spectroscopic measurements were performed in a transmission mode with the detection side being a large-area photodiode ($5.6 \times 5.6 \text{ mm}^2$) in contact with the sample. The detected signal was thus the diffusively transmitted light through the samples. The porous nature of the samples results in multiple scattering of the light, leading to exceptionally long path lengths of the injected light [13]. The pressure was controlled with the use of a vacuum chamber which was operated over a pressure range from 50 to 760 Torr.

III. RESULTS AND DISCUSSION

The absorption line profiles measured under ambient conditions are shown in Fig. 1. The HWHM of the absorption line of free O_2 was determined to be 1.58 GHz, in agreement with the expected value. The zirconia samples, with pore sizes of 43 and 115 nm, however, due to wall collisions, exhibit further broadened profiles, corresponding to HWHMs of $\Gamma = 2.69$ GHz and $\Gamma = 2.20$ GHz, respectively. In view of

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FIG. 1. (Color online) Comparison of the R9Q10 absorption line profiles of O_2 as free gas and in two ZrO_2 nanoporous materials with pore sizes of 115 and 43 nm under ambient conditions. It is clear that the absorption lines of the gas in the two nanoporous materials are significantly broadened as compared with the absorption line of the free gas. The insets show SEM images of the two nanoporous samples.

a mean free path of 60 nm for molecules in air at atmospheric pressure, a broadening is certainly expected [12]. The data presented in Fig. 1 show the potential of determining pore sizes nonintrusively. However, to obtain high sensitivity with respect to pore sizes, it is advantageous to perform measurements under reduced pressures. By reducing the pressure, broadening from intermolecular collisions can be suppressed, and, thus, broadening due to molecule-wall collisions is effectively more prominent. This can be seen in Fig. 2, where the measured HWHMs of the absorption lines of O_2 in the two nanoporous samples with different pore sizes are plotted against the pressure. It is seen that the relative broadening contrast between the two nanoporous materials increases with decreasing pressure. In addition, the trends of the absorption line broadenings of

FIG. 2. (Color online) Experimental data captured within the vacuum chamber showing the linewidths of the R9Q10 line of O_2 as a function of pressure. The solid line represents the predicted HWHM using a Voigt profile. Between the two nanoporous materials, the relative contrast in terms of broadening increases as the pressure is decreased. The trends of the nanoporous materials have close resemblances to the one of free gas, showing an additive-like behavior.

O_2 in the nanoporous samples closely resemble that of the free gas. This additive-like behavior suggests that it should be possible to consider the molecule-wall collision broadening to be only weakly dependent on the intermolecular collisions.

The increase in the broadening contrast of the absorption line is further illustrated in Fig. 3(a), where the line profiles of the nanoporous samples acquired under a pressure of 200 Torr are presented. Comparing the profiles under a reduced pressure and at ambient pressure (Fig. 1), the improvement in contrast is remarkable, in particular at the wings of the profiles (indicated by the dotted line at 10% of maximum value). The increased contrast will be of importance for pore-size determination of samples with similar pore sizes or for samples containing relatively large pores, where pressure broadening would otherwise be dominant. However, it is important to note that for measurements under a reduced pressure, the signal will be weaker due to the reduced number of absorbers and the signal-to-noise ratio will become a limiting factor for measurements at too-low pressures. Thus, while contrast is improved, a trade-off in finding suitable operating conditions must be found. In this study, an atmospheric gas mixture was used and the degradation in signal can, of course, be partly alleviated by using a pure O_2 atmosphere within the chamber.

Figure 3(a) also shows fits (dashed lines) using Voigt profiles for the 43-nm sample and for free gas. The Voigt fits

FIG. 3. (Color online) (a) Line profiles of the two ZrO_2 samples and of free gas at 200 Torr. Dotted lines show the half maximum value and the 10% of the maximum value, respectively. Compared with the line profiles under ambient conditions, the relative contribution from molecule-wall collision broadening is significantly larger under a reduced pressure, effectively enhancing the contrast between the two samples. The dashed lines indicate fits using Voigt profiles for the 43-nm sample and for free gas, showing that the molecule-wall-collision-broadened line shape deviates from a Voigt profile. (b) Residuals of the fit for the 43-nm sample.

were performed using a fixed Gaussian profile, corresponding to the Doppler broadening at 296 K, and optimization was performed with respect to the Lorentz profile. From the fits, it can be seen that while a Voigt profile can represent the absorption line shape of free gas very well, the molecule-wall-collision-broadened absorption line shape cannot be represented by a Voigt profile. The latter is further illustrated in Fig. 3(b), where the fit residuals for the perturbed case are shown.

The broadening of gas absorption lines is a topic which has been studied extensively. Under free-gas or free-gas-like environments, the main broadening effects are the pressure broadening and the Doppler broadening, which can be consolidated into a Voigt profile. Under confinement, however, the molecules will collide with the walls and become perturbed, resulting in further broadening of the absorption lines. The geometry of the confinement will determine the wall-collision rate, and it has been experimentally shown that the broadening exhibits a pore-size dependence [12,13,18,19]. Prediction of the total collision broadening of absorption lines is, on the other hand, highly nontrivial. In the microwave domain, wall-collision broadening has been studied under pressures in the mTorr range in cavities with dimensions in the cm range [20–22]. Similar to the results presented in this work, Luijendijk [21] has shown that wall-collision broadening, in the microwave domain, should not give rise to a Lorentzian line shape, in contrast to earlier works by Johnson and Strandberg [23] and by Unland and Flygare [24]. Furthermore, Luijendijk found that the total absorption line broadening could be approximately described by the additive behavior [21],

$$\Gamma_c = \Gamma_{\text{mol}} + r_0(r)\Gamma_{\text{wall}}, \quad (1)$$

where $\Gamma_{\text{mol,wall}}$ are the HWHMs due to intermolecular and molecule-wall collisions, respectively; $r_0(r)$ is a scaling factor relating the effective contributions from molecule-wall collisions and intermolecular collisions to the actual HWHM with $r = \Gamma_{\text{mol}}/\Gamma_{\text{wall}}$. While $r_0(r)$ may imply a complex relationship, it has been shown that $r_0(r)$ is a slow varying function, taking values of 0.79–1.2 for a large range of r values of 0.1–300 [21]. Both the mismatch between the Voigt profile and the experimental profile, as well as the close to additive-like behavior of the broadening effect, can be seen in Figs. 2 and 3, supporting previous results. It is, however, worth pointing out again that wall collisions in the microwave domain were studied in Ref. [21], and further investigations within the optical domain, for example, in terms of how the Doppler broadening couples into the total collision broadening and the validity of the model within the optical domain are certainly needed.

In the optical domain, collision broadening by foreign gases has, on the other hand, been extensively investigated. As discussed, the analysis of the line shape in Fig. 3 was based on the Voigt profile, which failed to describe the observed line shape. This can be attributed to the fact that the Voigt profile assumes that molecular collisions which lead to pressure broadening and shifts are velocity independent and that the molecules follow simple straight-line trajectories [25–27]. However, since the dimensions of the nanopores used

in this study are significantly smaller than the wavelength of the light, and the perturber mass, i.e., the walls, is much larger than the mass of the O_2 molecule, Dicke-type narrowing effects [28,29] may partly explain the deviation. Therefore, a future model could consider a velocity-changing effect, which primarily causes a contraction of the Doppler profile and will be of importance as the pressure is reduced (seen in Fig. 3). Several velocity-dependent models and corresponding profiles have been reported in the literature, with underlying physics that should also be relevant for wall-collision line broadening, such as the Galatry profile [30], Rautian-Sobelman profile [31], and the speed-dependent Voigt profile [25].

A point worth mentioning when using a vacuum chamber with reduced pressure is that it is a very gentle method to extract information regarding the pore structure. The samples used in this study had open pores leading to very rapid gas diffusion. However, for samples with an unknown pore structure, it is possible to determine whether the pores are open, i.e., have a gas exchange with the surrounding, by swiftly altering the pressure and comparing the obtained line profiles with those predicted by gas kinetics theory. In addition, the amount of mismatch between a measured line profile and a theoretical profile obtained based on a proper theoretical model provides information about not only whether closed pores exist but also the amount of closed pores relative to open pores.

IV. CONCLUSIONS

In conclusion, the work presented in this study represents an initial step toward understanding broadening of optical absorption lines due to wall collisions. In addition to being an interesting fundamental physics problem, the results also demonstrate that under reduced pressures, it is possible to sensitively assess the pore sizes of porous materials nonintrusively. Furthermore, we have shown that wall-collision broadening exhibits an additive-like behavior to the pressure and Doppler broadening effects and that the total wall-collision-broadened line shape clearly deviates from a Voigt profile. The possible causes of this deviation are discussed based on the physical effect of Dicke-type narrowing. However, large efforts most likely remain before the problem is fully understood. Currently, evaluation of pore sizes often involve complex or destructive methods. Provided a proper model for wall collisions, we envisage a significant impact within the fields of material analysis and material science for translucent porous materials. Such a model could be used to sense the predominant pore size nonintrusively. Using more refined models, it can even be possible to extract information regarding the pore-size distribution and the material structure.

ACKNOWLEDGMENTS

This work was supported by a direct grant from the Swedish Research Council and a Linnaeus grant to the Lund Laser Centre.

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