Spray-loading: A cryogenic deposition method for diamond anvil cell

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An efficient loading technique has been developed for flammable, toxic, or explosive gases which can be condensed at liquid nitrogen temperature and ambient pressure in membrane diamond anvil cells (DACs). This cryogenic technique consists in a deposition of small quantities of the desired gas directly into the sample chamber. The deposition is performed using a capillary that reaches the space between the diamond anvils. The DAC is kept under inert gas overpressure during the whole process, in order to avoid contamination from atmospheric O2, CO2, and H2O. This technique provides significant advantages over standard cryo-loading and gas-loading when the condensation of dangerous samples at liquid nitrogen temperature raises safety concerns because it allows dealing with minimum quantities of condensed gases. The whole procedure is particularly fast and efficient. The “spray-loading” has been successfully used in our laboratory to load several samples including acetylene, ammonia, ethylene, and carbon dioxide/water or red phosphorus/NH3 mixtures. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5011286

I. INTRODUCTION

Sample preparation in a Diamond Anvil Cell (DAC) represents a crucial part of high pressure experiments, and the loading procedures are often the most challenging tasks. Typically, solid and liquid samples can be directly loaded between the anvils, inside the gasket sample chamber, and the cell can be closed by applying external pressure. The entire operation can be executed using a microscope to visually inspect the sample, and the procedure can be conducted in a safe environment, for instance, by a glove-box. The loading of gaseous samples is instead much more complicated, and the good method to achieve it strictly depends on the thermodynamic and chemical properties of the gas itself. Generally, the idea behind the loading of gases is to condense them at a low temperature or at high pressure. In any case, it is mandatory to put enough matter between the anvils for preventing the closure of the gasket hole when external pressure is applied. The two main techniques to achieve these objectives are named cryo-loading (low temperature and low pressure) and gas-loading (room temperature and high pressure). Both these techniques require dealing with large quantities of condensed gases. Cryo-loading is used for gases with the boiling point and melting point, respectively, above and below 77 K,1 while gas-loading is employed for gases with the boiling point lower than 77 K, where the production of a sufficiently dense fluid to fill the sample chamber is needed.2 These efficient methods are widely used, but the main disadvantage emerges when dealing with dangerous chemical species, such as explosive (i.e., C2H2), toxic, or corrosive (i.e., NH3) gases. In fact, handling large amounts of these kinds of chemicals could be very dangerous for the operators as well as for the instrumental equipments. Moreover, cryo-loading is typically performed using liquid nitrogen baths, where the temperature is fixed to 77 K, or commercially available cryogenic baths, which typically allow controlling temperature only down to 223 K. If the gaseous sample solidifies in this temperature range, its solidification inside the cryogenic vessel may raise serious safety issues due to the blocking of in/out tubes. Furthermore, the solidification could prevent the mechanical closure of the cell. Finally, for the loading of mixtures of species having very different melting and boiling points, both these standard techniques are not suitable.

To overcome these limitations, and specifically for loading acetylene and ammonia, we have developed a novel technique that allows us to work with really small quantities of condensed gas, avoiding risks related to explosive, corrosive, or toxic chemical species, and to perform depositions of mixtures whose components are characterized by very different melting points. This technique is based on a cryogenic procedure aimed at performing an in situ deposition of the desired amount of condensed gas, by means of a capillary directly reaching the sample chamber of the DAC, delimited by the anvils and the gasket hole, and has thus been called spray-loading. The experimental apparatus is simple and easy-to-build, and we realized it with very low budget, exploiting the resources and the expertise of the European Laboratory for Non-Linear Spectroscopy (LENS) Mechanical Workshop.

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II. APPARATUS AND METHOD

The design criteria for our apparatus include (a) a thermally insulated cryogenic vessel with in/out access to let an inert gas flow inside the loading chamber at pressure higher than room pressure, thus avoiding contamination due to the atmospheric $O_2$, $CO_2$, and $H_2O$, and with an aperture for inserting the deposition capillary for the sample gas; (b) a direct measurement of the temperature near the diamond tips, to perform the deposition at the desired temperature conditions; and (c) the possibility to mechanically close the DAC before opening the vessel, to avoid both contamination and getting stuck due to the freezing of mechanical parts of the cell. The small and lightweight portable apparatus that was designed and built to match these criteria is shown in Figs. 1 and 2.

A more detailed scheme of the apparatus, providing actual dimensions as well as sideways and vertical hindrances, can be found in Figs. S1 and S2 of the supplementary material. In principle, to cool down the cell is possible by using both a liquid nitrogen bath in an inert atmosphere and a closed-cycle cryostat (whose use is mandatory when the condensation temperature is below 77 K). In our case, as we worked mainly on acetylene and ammonia, the apparatus consists of a cryogenic vessel kept under inert gas purging ($N_2$, Ar or He), where a specifically designed aluminum DAC holder is placed. The apparatus is designed for membrane Diamond Anvil Cells (mDACs), but it can work also for mechanical ones with suitable modifications. The box is covered by a Plexiglas cap, held between the poles of the DAC holder and the two handles of the whole structure, which allows us to easily remove it from the vessel once the loading procedure is completed. The DAC, slightly open with the diamonds spaced a few mm and the cover not completely screwed, is placed on the holder. On the metallic cover of the DAC (see details in Fig. 1), an eyelet has been mechanically perforated to let the deposition capillary reach the sample chamber through the spaced diamonds. The deposition capillary is a standard stainless steel 1/4-in. tube (internal diameter of 4 mm) welded to a thinner capillary (external diameter of 2 mm and internal diameter of 1 mm) where the tip hole has been closed by welding and a 1 mm gas outlet has been drilled perpendicularly to the flux direction so that, when the capillary is horizontally inserted into the DAC, the sample gas is sprayed directly over the bottom diamond (see Fig. 3). Purge gas flows inside the vessel through a 6 mm Rilsan® tube, while liquid $N_2$ is poured into the cryogenic vessel by a tunnel through a dedicated hole drilled in the Plexiglas cap. During the procedure, the liquid is normally poured inside the vessel until it reaches the base of the DAC. The temperature near the sample chamber is monitored via a thermocouple blocked on the backing plate where the diamond is mounted and connected to an external reader. The thermocouple wire exits from the bottom of the DAC through a dedicated channel milled on the DAC holder. A fork is blocked to the DAC cover by two grub screws. The cover is not completely screwed on the lower semicell so as to let the diamonds spaced and to put the oval opening in the correct position for the capillary to enter the DAC. Being known the exact number of turns that puts the cover in the loading position, as well as how many turns are necessary in total to bring the diamond tips in contact with the gasket, it is possible to close the DAC by screwing the fork of the exact number of turns actually necessary, avoiding any risk of overpressure and diamond damages during the closure. In this way, once the loading is completed, the deposition capillary can be extracted from the cell and, as previously described, turning the fork by its external handle allows us to mechanically close the DAC; then, pressure can be remotely applied to the membrane by the pressure driving...
The spray-loading technique, originally developed to be used in combination with a closed-cycle cryostat, allowed us to load several water/hydrocarbon mixtures. This method was extremely time-demanding due to the complex procedure for assembling the closed-cycle cryostat, mounting the DAC inside the cryostat, and pumping the whole system. Furthermore, access to the DAC was limited and every failed loading attempt would have meant to restart the whole complex procedure from the beginning. The new version of this apparatus, described in Secs. I–III, was instead developed to be simpler and easy-to-use, making the preparation step faster. The efficiency of the loading procedure can be highlighted by the IR spectra because, by probing all the samples at once, they provide information about any possible sample contamination.

Acetylene is the simplest alkyne, a highly unstable molecule that requires special care to be handled, because it is explosive (especially if pressurized) and highly flammable. Commercial acetylene is indeed supplied and stored dissolved in acetone. The loading of \( \text{C}_2\text{H}_2 \) (Rivoira, purity of 99.6%) and further purified prior to loading is performed by realizing the deposition between 195 and 185 K since the acetylene melting point is at about 191 K. In addition, special care must be taken to avoid that the pressure applied during the closure of the DAC would overcome the relatively low pressure reaction threshold for pure acetylene to polymerize (about 4 GPa at room conditions). In Fig. 4, a Fourier-transform infrared (FTIR) spectrum of a sample of acetylene loaded with spray-loading is shown. The spectrum is dominated by the infrared allowed \( \nu_1 \) (antisymmetric C–H stretching) and \( \nu_3 \) (antisymmetric C–H bending) modes, respectively, at 3250 and 750 cm\(^{-1}\) and by the \( \nu_4 + \nu_5 \)
combination mode at about 1365 cm$^{-1}$ (where $v_4$ refers to the C–H symmetric bending). All these modes are out of scale. The combination bands for acetylene are visible at much higher frequency. No traces of atmospheric water or CO$_2$ can be detected in the spectrum, attesting for the complete absence of contamination in the loaded sample. We loaded with this method several samples of pure C$_2$H$_2$ and C$_2$H$_5$ in the presence of 3D and 1D pure SiO$_2$ zeolites for studying its polymerization reaction under extreme confinement.$^{8,9}$

Ammonia is irritant and corrosive. In fact, as a corrosive species, ammonia could be dangerous to load for the typical cryo-loading instruments, aside from being dangerous also for some components of the DAC (Cu components especially, such as copper rings used for mounting anvils on the backing plates, which need to be protected by using resins or specific glues). In our experiments, ammonia was loaded by performing the deposition at about 195 K, thus just below the melting point. In this case, unlike in the acetylene loading, no special care is needed for what is concerned with the pressure of the DAC after the loading and during the warming to ambient temperature because of the chemical stability of pure ammonia. In Fig. 5, a FTIR spectrum of a sample of NH$_3$ loaded by the spray-loading technique is shown. The inset picture shows the aspect of the sample, and two ruby chips are visible on the edge of the gasket. The spectrum is dominated by the out-of-scale $v_2$ (symmetric N–H bending, 1060 cm$^{-1}$), $v_1$, $v_3$ (symmetric and doubly degenerate N–H stretching, at about 3300 cm$^{-1}$), and $v_4$ (doubly degenerate N–H bending, 1630 cm$^{-1}$) infrared allowed modes. The combination bands of NH$_3$, $v_2 + v_3$, and $v_3 + v_4$ are visible at higher frequencies.$^{10}$

No evidence of the contamination of the as-loaded sample due to atmospheric water or CO$_2$ can be seen in the spectrum. We loaded with this method several samples of pure NH$_3$ and heterogeneous mixtures of NH$_3$ in the presence of graphene oxide$^{10,11}$ or red phosphorus for structural and reactivity studies.

The spray-loading technique and apparatus can be profitably used to load mixtures of species with very different melting and boiling points. In our laboratory, we developed a dedicated deposition line for mixtures containing water, and recently we have studied carbon dioxide/water mixtures. The DAC was prepared with rubies and cubic Boron Nitride (c-BN) as independent pressure gauges and then mounted on the spray-loading aluminum holder. Carbon dioxide (Rivoira, purity of 99.99%) served at the same time as one of the mixture components and as a gas carrier to gurgle through a glass bottle of ultra-pure water so as to transport small water droplets with its flux. The two components did condense directly into the sample chamber when the temperature of the DAC reached 193 K. For cooling down the DAC, we used a liquid nitrogen bath. During the whole procedure, a small flux of He was maintained through the line so as to keep the deposition capillary warm: in the case of this mixture, in fact, an additional issue is related to the presence of water in a very low temperature environment. Water could freeze along the line, resulting in a stuck of the small aperture of the deposition capillary. In addition, the deposition capillary itself, the bottle of water, and most of the loading line are kept under moderate heating during the whole procedure. At the end of the deposition, the top diamond is directly frozen down using liquid nitrogen prior to the mechanical closing of the cell, so as to avoid that a temperature gradient on the diamond tips could result in an undesired melting of the mixture while sealing the sample chamber. Figure 6 reports a FTIR spectrum of the mixture of carbon dioxide and water loaded as described. The infrared absorption modes of water (bending, 1645 cm$^{-1}$, and stretching, 3300 cm$^{-1}$) dominate the spectrum. As the CO$_2$ phase I is concerned, the saturating bending (around 660 cm$^{-1}$), the stretching (around 2345 cm$^{-1}$), and the combination $v_3 + v_1$, $v_3 + 2v_2$ (with major peaks at 3610 and 3730 cm$^{-1}$) regions are clearly visible. All these absorption bands are out of scale. More details about the assignments can be found in Refs. 12 and 13. The picture in the inset shows the aspect of the sample. Pressure gauges (round-shaped rubies and a triangle-shaped crystal of c-BN) are clearly visible in the sample chamber.
V. CONCLUSIONS

We have discussed the construction criteria of a novel, useful apparatus to perform cryogenic deposition of gases inside the DAC. This method can be profitably used for potentially hazardous samples (explosive, toxic, or corrosive ones with condensation temperature above 77 K) and for the loading of complex mixtures of gases and chemical species with very different melting and boiling points. Spray-loading allowed us to obtain several samples of acetylene, ammonia, and ethylene in the DAC simply by the condensation of a small quantity of gas directly inside the sample chamber. The method allowed us to load pure gaseous samples and also composite samples (solid and fluid mixtures, where the solid components were loaded before the DAC was placed in the cryogenic vessel). The loading procedure is fast and efficient and, due to the small dimensions and the portability of the experimental apparatus, can be performed under hood without any risk. Spray-loading has been demonstrated to be a suitable and useful technique for the loading of hazardous samples and very complex mixtures of different species.

SUPPLEMENTARY MATERIAL

See supplementary material for a complete description of the experimental equipment with sizes and a list of the fabrication materials.

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