A high pressure cell for dynamic light scattering up to 2kbar with conservation of plane of polarization

by

G. Meier and H. Kriegs

Institute of Solid State Research, (soft matter), Research Center Jülich, POB 1913,

52428 Jülich, Germany

Abstract

We report on a high pressure cell with 6 optical windows which can be used up to 2kbar for laser light scattering applications at scattering angles of 45°, 90° and 135° of liquid samples in a temperature range between –20°C up to 150°C. The pressure transmitting medium is compressed nitrogen. The window material used is SF57 NSK, a glass with an extremely low stress optical coefficient in the order of about 10^{-5} which allows thus to maintain the plane of polarization even under the action of high pressure. In order to demonstrate the functioning of the cell we show Rayleigh-Brillouin spectra of poly(methylphenylsiloxane), PMPS, at different polarizations and pressures.

Introduction

The use of optical cells for high pressure applications is an on going field in soft matter physics. Pressure is an often wanted but rarely used physical parameter since for obvious reasons its applicability is much more complicated than temperature for example. High pressure optical investigations need windows through which light is passed. However, there is no ideal window material available. Either the windows are pressure resistant like fused silica, however, with some inherent birefringence or sapphire with optical disadvantages (sapphire is a perfect polarization scrambler) or they are optically favorable like glass but not very pressure resistant. Therefore very few optical high pressure cells for depolarized scattering have been reported[1,2]. On the other hand, the possibility of measuring the depolarized intensity is highly desirable, because in light scattering polarized intensity and depolarized intensity are of different molecular origin and hence its analysis gives access to different physical quantities. However, we are not aware of any cell which can routinely be operated for this purpose. The basic drawback is the proper use of the window material. Cantor et al.[3] have reported that PPG float glass is a material with a very low Pockels coefficient P_{44}, lower than fused silica and recommend the use of ordinary float glass for optical high pressure cells. The polarization scrambling of this glass was found to be in the order of $3x10^{-3}$ up to 2kbar. Silica as window material was used by Fröhlich and Posch[4] in their cell up to 1.8kbar, however, they found pressure induced birefringence at those high pressures. Later Versmold[5] has reported a cell to measure the depolarized scattering from super critical CO_2 up to 1kbar using the glass SF57 which was exposed to a special cooling program such that P_{44} is minimized. The use of SF57 with special cooling seems to be the optimal choice. We have built and used the cell we report on here, in various cases both in VV and VH applications, where VV means vertically polarized incident light with regard to the scattering plane and

also scattered light in this direction and VH means then horizontally scattered light respectively. Originally the cell was constructed and first used[6] at the institute for Physical Chemistry at the University of Bielefeld, where the early papers[7] appeared. Later it was transferred to the Max-Planck Institute for Polymer Research Mainz, where first polymer mixtures under high pressure[8,9] and the dynamics of glass forming liquids have been studied[10-15]. The cell is now in two optimized copies of the old design in operation at the Biophysics lab at the University of Poznan and at the Institute of Solid State Research in Jülich as a joint experimental set-up. We are mainly concerned with the dynamics of glass forming liquids[16-19] and have optimized the apparatus for interferometric investigations, in our case a Sandercock triple-path tandem interferometer, however, also purely high pressure photon correlation work is reported[20] on colloidal systems. In this paper we use as an example for the Rayleigh-Brillouin spectroscopy the amorphous transparent polymer poly(methylphenylsiloxane) PMPS, which was synthesized at the Max-Planck institute for polymer research in Mainz[21]. PMPS possesses a noticeable depolarized intensity[22] and can thus be well used to show both the longitudinal and transverse phonon propagation as a function of pressure[23]. We have optimized the experimental conditions for the interferometric work, thus a simultaneous investigation by means of photon correlation spectroscopy does not make sense because of the different time windows of both methods. An interferometric investigation under the action of pressure in viscous systems with inherent anisotropy is the best imaginable test case for the use of this cell as a high pressure device suitable for light scattering with the aim of conservation of the plane of polarization. The reason is buried in the fact that the appearance of inelastic modes, the longitudinal acoustic phonons (LA) and the transverse acoustic phonons (TA) in the measured spectra $I(\omega)$ are extremely sensitive markers for the correctness of the polarization settings as the TA phonons only appear in the VH mode. Such a test would not be possible to perform with photon correlation spectroscopy also for the reason that in the long time limit all processes in glasses are somehow correlated and thus no

clear molecular assignments can be done. The measurement of the photon correlation from the high pressure set-up, which is used for interferometric work, needs the sample cooled to slow down the relaxation processes such that they fit to the time window of the correlator. This data has already been taken and is published by Kriegs et al.[17]

Technical Aspects

1.The cell as hollow cylinder: General layout and stability

In Figure 1 the general layout is shown as a cross section from top to bottom through the middle of the cell. It is constructed from stainless steel 1.4057 (X22CrNi17). We see the main pressure inlet from the top, which is provided as an inlet of nitrogen through a standard high pressure connector which is build in a large central screw serving as closing to the main cell body via an O-ring. The cell has a jacket through which a liquid is pumped to assure a certain measurement temperature. We can reach temperatures down to –25°C using ethanol and temperatures up to 150°C using polyethylene glycol. If one uses the cell at low temperatures one needs to cover the cell with a box in which dry nitrogen is blown in order to prevent the condensation of moisture on the windows. The accessibility of different temperature ranges depends on the O-ring used. For measurements at temperatures below 10°C a Kalrez ring is used since it does not shrink significantly, whereas for measurements at higher temperatures a Viton ring was found to be sufficient. Figure 2 shows a cross section through the cell on the level of the windows. It indicates the configuration of the 6 optical windows, the led through for the thermocouple (Ni-CrNi) and the additional connector for the rupture disk fulfilling the safety requirements. The window assembly is sealed against the cell by an O-ring in a similar way as the central top screw. All plugs are build in using copper paste to avoid screw-seizing. The stability of the high pressure vessel is calculated to a good approximation by assuming that the cell can be considered as a thick-walled hollow cylinder with end caps. The relevant

mechanical quantity to judge the stability of such an device under the action of an internal high pressure is the effective stress σ_{eff} at the inner borehole. We would have deformations if σ_{eff} is larger than the value of the yield strength of the steel used which is in this case 475N/mm^2. The relation between σ_{eff} and the geometry of the cell as a function of the radius r for a given pressure is

$$\sigma_{eff} = \sqrt{3}\frac{a^2 b^2 P}{\left(-b^2 + a^2\right)}\frac{1}{r^2} \qquad \text{eq. 1)}$$

where 2a is the inner hole diameter , 2b the outer cell diameter and P is the pressure. In the geometry given (a=10mm, b=72mm, yield stress=515N/mm^2 at T=50°C, 475N/mm^2 at T=150°C, low temperature values not known) we can calculate that the yield stress of the steel is reached at a pressure of P=260N/mm^2. Using a safety factor of 1.3 we can therefore assure safe operation up to 200N/mm^2 which is 2kbar.

In this calculation no corrections for bores and other drillings have been used. However, a finite element analysis of the cell which was kindly performed by Dr. H. Cords from the Central Technology Division at the Research Center in Jülich showed that the cell with all modifications is safe up to 2.25kbar. More important is the fact that the finite element analysis showed that the horizontal beam channels do cause localized stress concentrations which, however, do not lead to a mechanical breakdown of the cell. Crucial points are the cutting edges of the cut out diameters, however the maximum stress did not exceed 490N/mm^2 which is still in the range of plastic stretching.

2. The optical window construction

The pressure stability of the window construction is not implemented in the calculations. The technical details are shown in Figure 3. The glass basically sits on a very flat machined surface, which has a surface roughness in the order of 2μm. In order to be on the safe side with regard to a possible point load due to imperfections or spurious impurities we use a Teflon foil in form of a ring of 20μm thickness between glass and metal. We produce the ring of proper diameters by stamping it out from the foil thereby taking care that the edges really are smooth. Otherwise additional local point loads can occur leading to window crack. In order to also have the cell gas tight at low pressures we press the glass on to the hub by means of a cap which tightens via an O-ring at the 45° bevel of the window. In contrast to the mechanical characteristics of the steel used, we do not have any decent values for the mechanical stability of the glass used. Therefore we had tested the window construction shown in Figure 3 in a test device and found no crack of the window construction for pressures up to 3kbar.

3. The use of nitrogen as pressure transmitting medium

We have chosen compressed nitrogen as the pressure transmitting medium mainly for the reason that then the medium separation of the sample from the pressure transmitting material is most simple. Nitrogen is compressed by a Nova-Swiss membrane compressor reaching a maximum pressure of 3kbar. However, compressed gases store a lot of kinetic energy and care must be taken. On the other hand nitrogen diffuses into the sample and one has to estimate how long that takes under various conditions. Diffusion coefficients of gases like nitrogen, oxygen etc. in simple liquids lie in the order of $D = 2x10^{-5}cm^2/s.$ at ambient pressure. Considering our sample positioning into the high pressure cell, the nitrogen must diffuse about x = 3cm to reach the laser beam position. Using $x^2=2Dt$, we estimate the time t for the nitrogen to reach the measuring position to be in the order of 2.6 days. This value will

even increase, because the action of pressure will decrease the value for D. Furthermore, if viscous liquids are studied, then a much lower value for D is also found thus extending the range of measurability.

The optical Set-Up used

In Figure 4 we show the optical set-up used for all our measurements with the high pressure cell. To assure a clean polarization we use Glan and Glan-Thomson prisms from Halle, Berlin which are specified to a rejection ratio $1:10^7$. By that arrangement the polarized (VV), depolarized (VH) spectra was obtained. The set-up for interferometric measurements at $\theta = 90°$ is shown in Fig.4. For interferometric backscattering measurements a somewhat different light path must be used. This is also shown in Figure 4, indicated by the dotted light path. In backscattering a small ($2x2mm^2$) rectangular prism is used to direct the beam into the cell. The aperture from the optical window of the cell is very small. Nevertheless the small prism causes only a rather small reduction of intensity in this geometry. Scattered light is fed into the entrance pin hole of the tandem interferometer.

It is possible to simultaneously perform photon correlation spectroscopy at scattering angles of $\theta = 45°$, 90° or 135° in the polarized or depolarized mode. We use a mono-mode fiber to collect scattered light. Either a photo multiplier tube PMT or an avalanche photo-diode APD acts as fast photon counting device. A multiple tau correlator with fast channels in pseudo cross correlation calculates the intensity autocorrelation function starting at a sample time of 6.25ns.

The sample Poly(methylphenylsiloxane) PMPS

The amorphous, transparent polymer PMPS was synthesized at the MPI-Polymerforschung in Mainz using standard a anionic polymerization procedure and was kindly supplied by Thomas Wagner. The material has a M_w of 12000D with a polydispersity index of 1.05 and a glass transition temperature of –27°C as determined by differential scanning calorimetry at a heating rate of 10K/min. The index of refraction n is 1.551. We use PMPS for our studies because it is perfectly amorphous, easy to prepare, all relaxation processes lie in a proper temperature and pressure range, it possesses an optical anisotropy due to the phenyl rings and thus gives rise to a depolarized intensity[22] and last but not least a large amount of data has been published using this material[17] especially in the very first paper using this cell by Fytas, Meier and Dorfmüller[4] in 1985, however, in that paper no depolarized data was shown.

Rayleigh-Brillouin spectra at high pressures

Since we are basically concerned with the suitability of our cell for high pressure applications, we have in a first step measured the depolarization $\delta = I_{VH}/I_{VV}$ (depolarized intensity scaled with the intensity obtained in VV geometry) of the cell in transmission by passing the laser beam through in VH configuration without any sample in the cell. Intensities were measured with a power meter (Coherent Field Master GS). At P=1bar we have obtained a value of δ of $2x10^{-5}$, which increased to $6x10^{-5}$ at P=1600bar. This is shown in Figure 5. Hence the depolarization due to the optical windows is very small and about two orders of magnitude

smaller than that which has been reported so far for other window materials. However, there are windows, which are not perfect with regard to depolarization. Typically there, the depolarization is in the order of 10^{-3} and thus only slightly better than in other materials. We have plotted in Fig. 5 the best obtained result. In order to show how these values of the depolarization (between 10^{-3} worst case to10^{-5} best case) influence the spectrum of PPMS at various pressures, we have performed measurements of the Rayleigh-Brillouin spectrum at two pressures ,920bar and 1610bar in VH geometry and in VV for comparison at a temperature of T=22°C. As the influence of VH on the VV spectrum is much smaller than vice versa, because the depolarized intensity is about a factor of 20-30 lower than the VV intensity, we only show the VH spectra as a function of pressure in Fig. 6.

Here we notice already a noticeable distortion of the measured VH spectrum. We can easily identify in the VH spectra the "leakage" of the LA phonons, which appear as small humps at the frequency positions which are known from literature[6]. We fit these VH spectra with two Lorentzians for the TA phonons and, in addition to that, two Lorentzians taking care of the LA distortion. The amplitude ratio between TA/LA phonons leads to a depolarization ratio which is also plotted in Fig.5. As an important result one can see that although the depolarization is low (10^{-3}) the effect on the spectrum is marked. We have therefore selected a perfect pair of windows and have repeated the measurements at P=920bar and P=1610bar. We show in Figure 7 the comparison between the undistorted curve at P=920bar with the non-perfect, distorted one at the same pressure.

As expected no LA phonon is observed even at that pressure. Since a spectrum, which can be as a first good approximation described only of two Lorentzians (plus quasielastic contributions) can not be fitted (model fit function is convoluted with experimentally determined resolution function) with four Lorentzians (two additional Lorentzians due to depolarization leakage) we have to conclude that the obtained depolarization δ is in the order of a few 10^{-5} and thus so small that true spectra, true in the sense of clean polarization, can be

obtained for pressures up to about 2kbar. Such a cell has not been reported for use in light scattering so far.

Conclusions

We have constructed a high pressure cell suitable for light scattering applications. The cell allows a pressure variation up to 2000bar in a temperature range –25°C to 150°C. It is equipped with 6 optical windows, which allow angular dependent measurements at 45°, 90° and 135° scattering angle. The glass used in the window construction has a very low stress optical coefficient and thus allows to perform high pressure experiments with the preservation of the plane of polarization. The best experimentally obtained depolarization is in the order of $3x10^{-5}$ for pressures up to 1600bar. We have demonstrated the applicability of the high pressure cell in performing Rayleigh-Brillouin measurements with a tandem Fabry-Perot interferometer on a polymeric material poly(methylphenylsiloxane), PMPS, which reveals longitudinal and transverse acoustic phonons depending on polarization. For the low reported depolarization of the glass windows unperturbed spectra of the transversal phonons in PMPS could be obtained for pressures up to 1620bar. We show further that the implementation of the cell into the interferometric set-up can also be realized in backscattering geometry, which allows us to separate the propagating modes in viscous liquids from orientational modes[23]. Besides the interferometric applications high pressure photon correlation spectroscopy is also possible[17,20].

Acknowledgement

We are indebted to Prof. H. Versmold for pointing out the window material to us. We thank the machine shop and the construction department of the IFF.

References

1. P. Bezot, C. Hesse-Bezoz and P. Pruzan, *Can. J. Phys*. **61**, 1291 (1983)
2. G. Pratesi, A. Bellosi and F. Barocchi; *Eur. Phys. J. B* **18**, 283 (2000)
3. D. M. Cantor, J. Schroeder and J. Jonas; *Appl. Spectros*. **29**, 393 (1975))
4. P. Fröhlich and H. A: Posch; *J. Phys.E. Sci. Instrum*. 12, 170 (1979)
5. H. Versmold; *Mol. Phys.* **43**, 383 (1981)
6. G. Fytas, G. Meier and Th. Dorfmüller; *Macromolecules* **18**, 993 (1985)
7. D. Lilge, W. Eimer and Th. Dorfmüller; *J. Chem . Phys*. **86**, 391 (1987)
8. M. Beiner, G. Fytas, G. Meier and S. Kumar; *Phys. Rev, Lett*. **81**, 594 (1998)
9. M. Beiner, G. Fytas, G. Meier and S. Kumar; *J. Chem .Phys.* **116**, 1185 (2002)
10. A. Patkowski, M. Matos-Lopez and E. W. Fischer; *J. Chem. Phys.* **119**, 1579 (2003)
11. A.Patkowski, M. Paluch and H. Kriegs; *J. Chem. Phys*. **117**, 2192 (2002)
12. L. Comez, D. Fioretto, H. Kriegs and W. Steffen; *Phys. Rev.E* **66**, 032501 (2002)
13. M. Paluch, C. M. Roland, J. Gapinski and A. Patkowski; *J. Chem. Phys*. **118**, 3177 (2003)
14. L. Comez, S. Correzzi, D. Fioretto, H. Kriegs, A. Best and W. Steffen; *Phys. Rev. E* **70**, 011504 (2004)
15. C. Dreyfus, A. Aouadi, J. Gapinski, M. Matos-Lopes, W. Steffen, A. Patkowski and R. M. Pick; *Phys. Rev. E* **68**, 011204 (2003)
16. A. Patkowski, J. Gapinski and G. Meier; *Coll. Polym. Sci*. **282**, 874 (2004)
17. H. Kriegs, J. Gapinski, G. Meier, M. Paluch, S. Pawlus and A. Patkowski; *J. Chem . Phys.* **124**, 104901 (2006)
18. A. Patkowski, J. Gapinski, G. Meier, H. Kriegs, A. leGrand and C. Dreyfus, *Europhys. Lett.* **73**, 607 (2006)
19. A. Patkowski, J. Gapinski, G. Meier and H. Kriegs; *J. Chem. Phys.* **126,** 014508 (2007)
20. G. Meier, J. Kohlbrecher, R. Vavrin, J. Buitenhuis, M. P. Lettinga and M. Ratajczyk; *Meas. Sci. Technol.*, **19**,0000 (2008)
21. B. Momper, Th. Wagner, U. Maschke, M. Ballauff and E. W. Fischer; *Polym. Commun.* **31**, 186 (1990)
22. G. Fytas, A. Patkowski, G. Meier and E. W. Fischer ; *Macromolecules* **21**, 3250 (1988)
23. H. Kriegs, J. Gapinski, G. Meier and A. Patkowski; *J. Chem . Phys*.; **127**, 0000 (2007)

Fig.1: Cross section from top to bottom through the middle of high pressure cell. 1: window assembly. 2: surrounding jacket. 3: cell body. 4: thermocouple assembly. 5: cell holder. 6: pressure in and out. The window assembly is explained in more detail in Fig.3.

Fig.2: Cross section of high pressure cell through level of windows. Assignments as in Fig.1. In addition 7: Connector for rupture disk. In the figure all windows are drawn in the physically correct positions, that is opposite to each other in pairs.

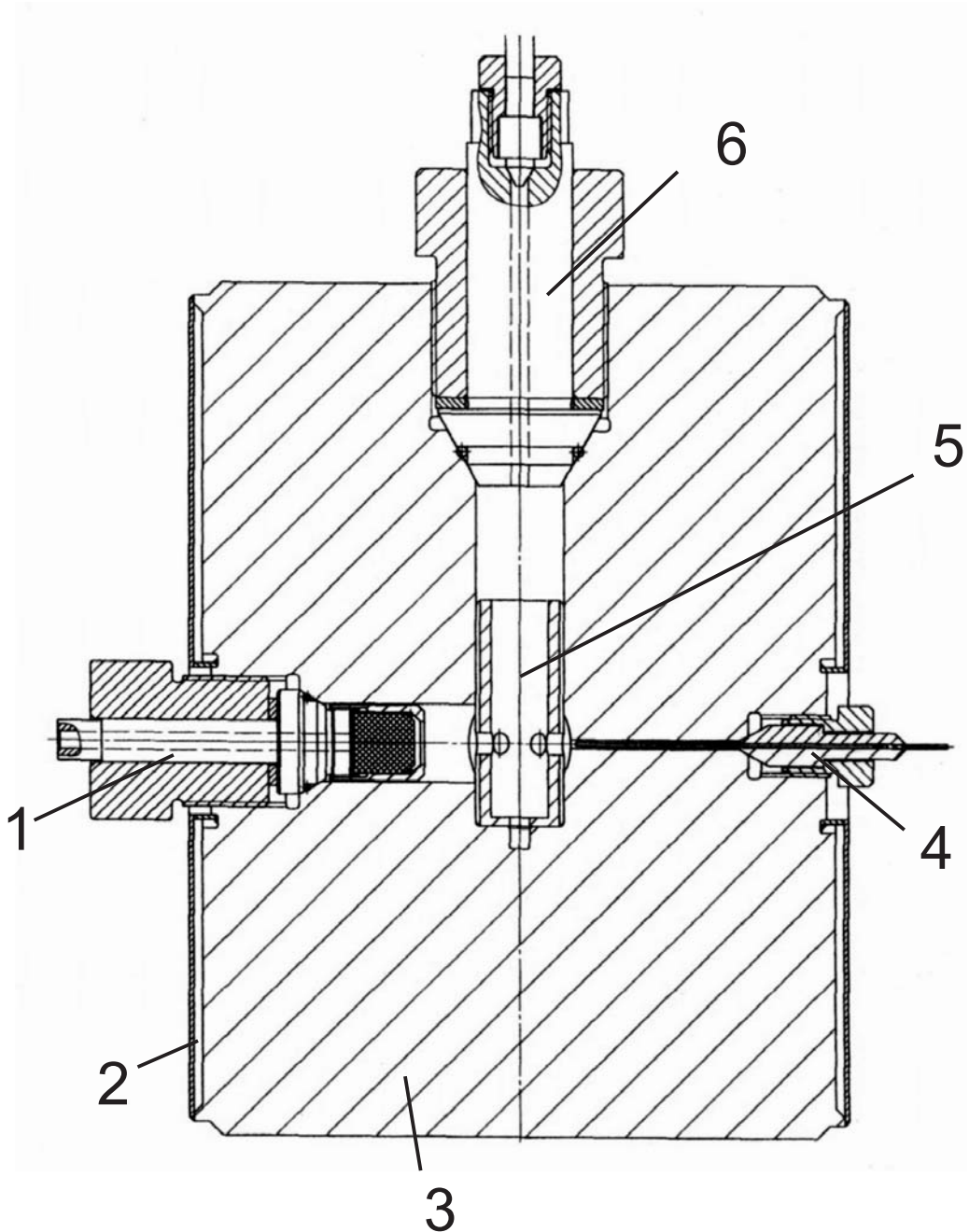
Fig.3: Details of window assembly: The main idea of the cap is to have the cell tight even at very low pressures. Via the cap one can press the window slightly on to the extremely flat surface of the window support device. At high pressures then the construction seals itself through the action of the internal pressure. 1:Supporting plug to held the window support device in place. 2:Brass ring. 3:Window support device. 4:Teflon foil. 5:Cap to press the window on 3. 6:O-ring. 7:Optical window. 8:O-ring.

Fig.4: Sketch of set-up including the possibility of performing backscattering experiments. The apertures of the high pressure cell are not in scale (exaggerated size). Alignment beam is necessary to define the optical axis for the tandem and defines the scattering center. Reference beam is needed for the internal stabilization of the tandem. MCA: multi-channel analyser to record the spectrum.

Fig.5: Measurement of the depolarization δ caused by the high pressure windows in transmission with crossed polarisers. The lower curve is the best obtained result and δ is in the order of 10^{-4} - 10^{-5} . The two points in the upper part of the figure are obtained from fitting VH curves shown in Fig.6 with a Lorentzian fit. The amplitude (of the Lorentzian contribution) of the TA phonon in the VH spectra compared to the TA phonon leads to the two values for the depolarization. These values have to be considered as typical and will be obtained if no special selection of the windows is performed. Nevertheless these values are already a factor of 2-3 times better than that which has been reported so far from other materials[3].

Fig.6: Pressure variation of the transverse acoustic phonons in PPMS at T=22°C. Data taken in VH geometry. Data with least TA phonon shift at P=1bar, then P=921bar. Data with largest phonon shift at P=1610bar. One can see the distortion of the spectra due to the appearance of the longitudinal acoustic phonons especially on the Stokes side of the high pressures at about 10-11GHz.

Fig.7: Comparison of VH spectra taken at P=920bar for PMPS with depolarization in the high pressure windows of about 10^{-3}, upper curve and the best obtained depolarization from the windows in the order of 10^{-5}, lower curve. Here no indication for a "leakage" of the VV longitudinal phonon can be seen. Upper curve shifted by a factor of 5 for reasons of clarity. Full lines are fits to the data, see text.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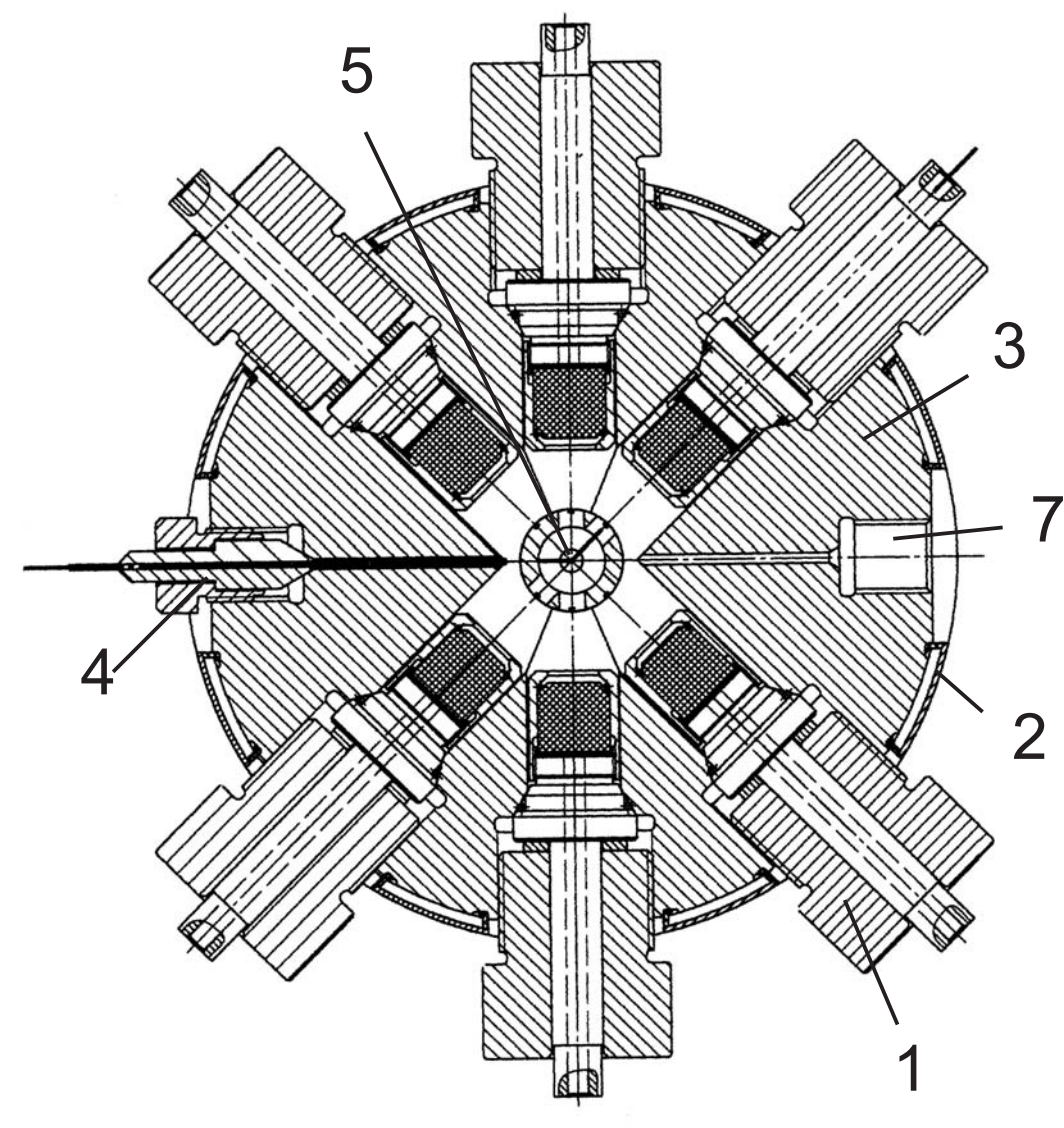
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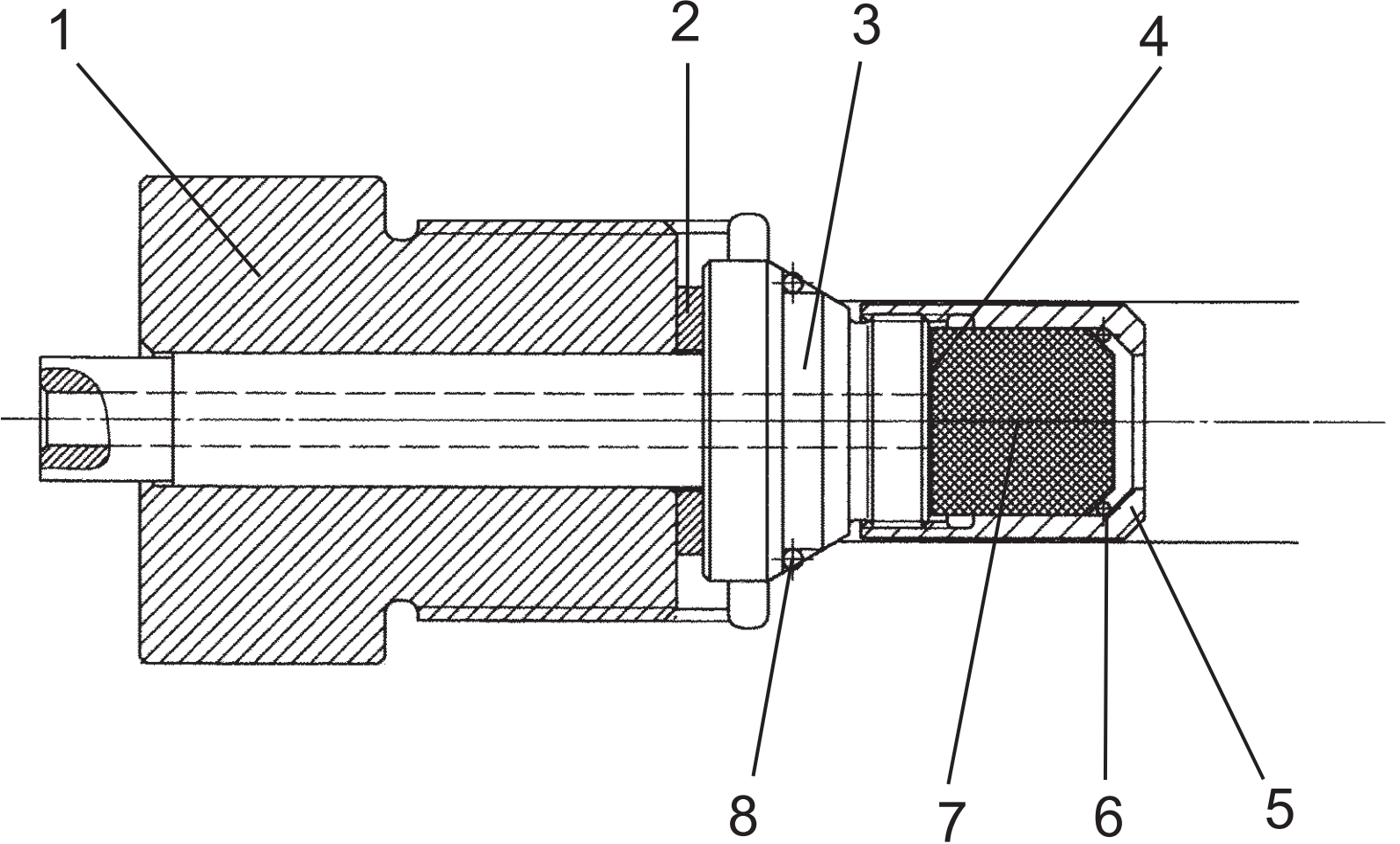
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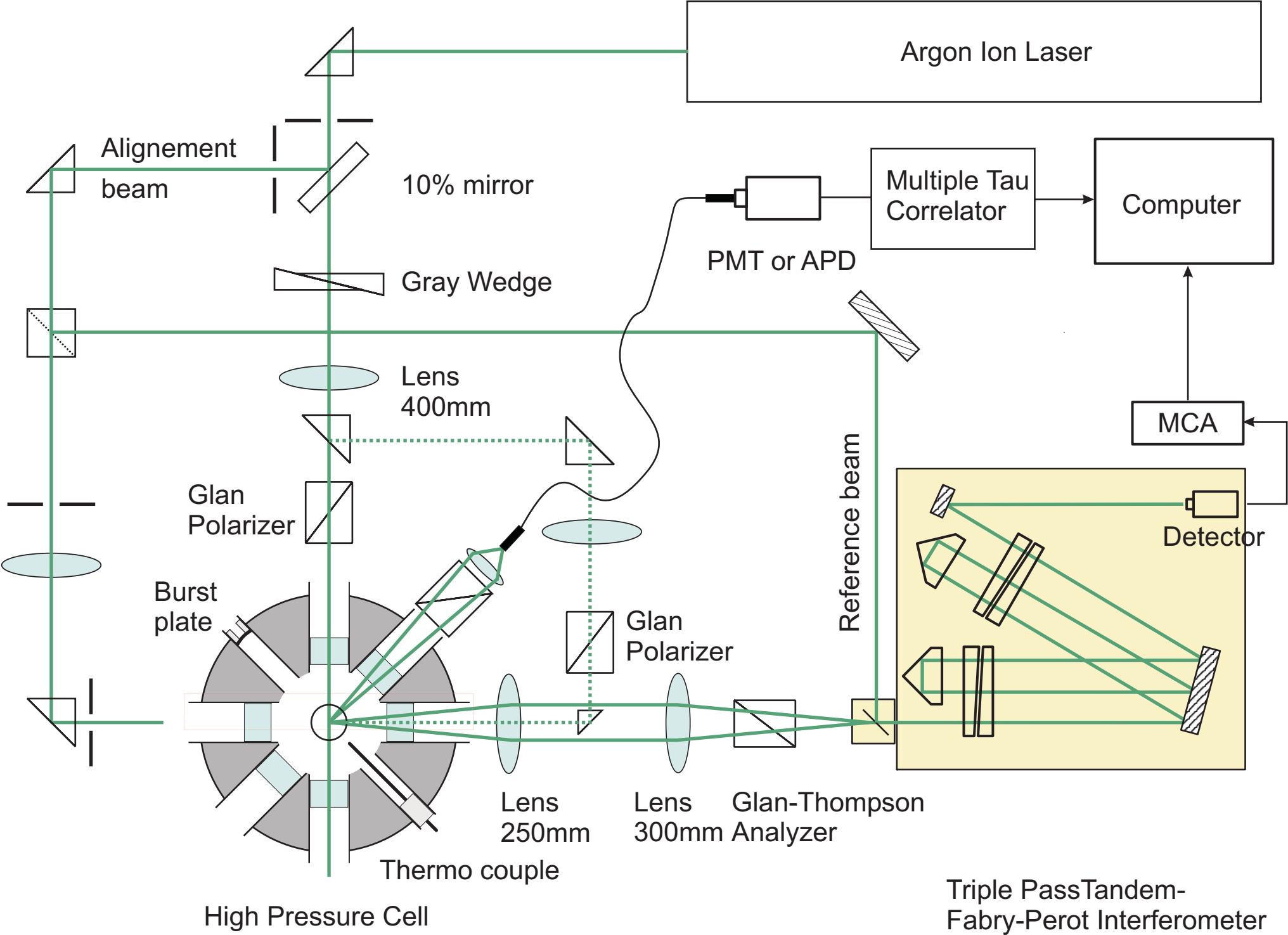
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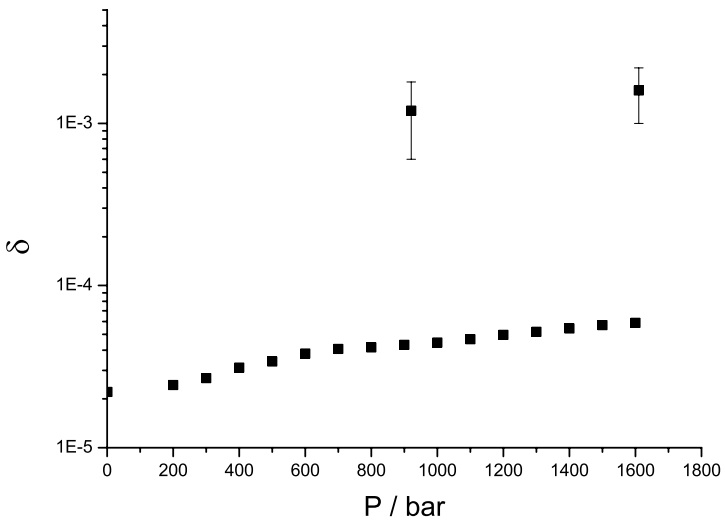
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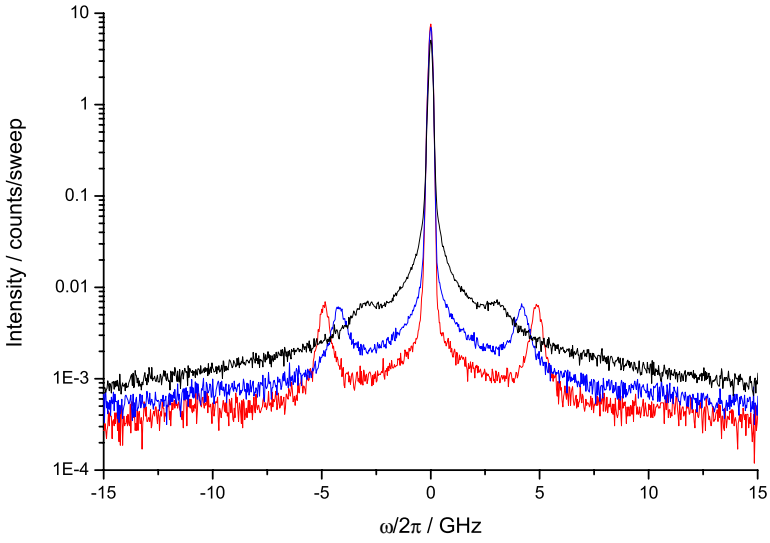
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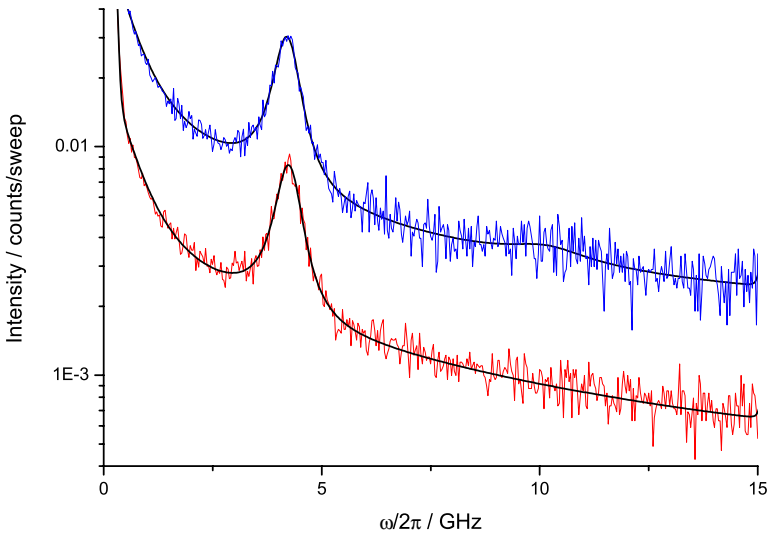
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