

DISPERSION GAS BAROMETRY

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Mechanical pressure limits

The pascal realized $p = F/A$ has practical limits set by mechanics. Take the example of the piston gage:

- At $p < 0.1$ MPa, the force F is uncertain because the buoyancy corrections for composite masses are not well known.
- For $(0.1 < p < 1)$ MPa, the area A is uncertain because a cylinder can not be dimensioned better than a few tens of nanometers.

- As $p > 1$ MPa, the area incurs additional uncertainties related to distortion, because there is doubt about the pressure distributed along the flanks of the cylinder.

After 150 years of refinement, further effort tackling these practical limits will yield minimal gains.

Optical pressure scale

- An alternative route to the pascal is the ideal gas law

$$p = \rho RT, \quad (1)$$

which defines pressure as density ρ at a known temperature T ; R is the molar gas constant.

- Modern thermometry places a $0.5 \mu\text{Pa}/\text{Pa}$ limit on this thermodynamic definition—an order of magnitude more accurate than practical limits on the mechanical definition.

- Density may be accessed via the Lorentz–Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = A_R \rho. \quad (2)$$

So, $\rho \approx \frac{2}{3A_R}(n - 1)$ and the density limit on (1) is either the measured refractivity $n - 1$ or knowledge of the molar refractivity A_R .

- Molar refractivity

$$A_R(\nu) = A_\epsilon + A_2\bar{\nu}^2 + A_4\bar{\nu}^4 + A_6\bar{\nu}^6 + A_\mu, \quad (3)$$

has $A_\epsilon \equiv \frac{4\pi}{3}N_A\alpha$ from static polarizability α and $A_\mu \equiv \frac{4\pi}{3}N_A\chi$ from magnetic susceptibility χ , with the Avogadro constant N_A . The Cauchy coefficients $A_{2,4,6}$ describe polarizability dispersion as a function of reduced frequency $\bar{\nu} \equiv \nu/(10^{14} \text{ Hz})$, with $\nu = c/\lambda$ given by the speed of light in vacuum divided by wavelength.

- Helium is the gold standard thermometric gas: *ab initio* calculation provides uncertainty below $10^{-7} \cdot A_R$.

- The limit realizing (1) is measurement of $n - 1$, which has large uncertainty caused by distortion of the optical device as it is filled with gas.

- When measuring helium $n - 1$, the inaccuracy of a refractometer is about 1000 times larger than uncertainty in the calculated A_R .

Principle of dispersion gas barometry

- An FP cavity refractometer measures $n - 1 \approx -\Delta f/\nu + \kappa p$, where $\Delta f/\nu$ is the fractional change in cavity resonance frequency as gas is added, and κ is the distortion coefficient. From (1) and (2), $n - 1 \approx 3A_R\rho/(2RT)$, so

$$p \frac{3A_R}{2RT} = -\frac{\Delta f}{\nu} + \kappa p. \quad (4)$$

- If refractivity is simultaneously measured at disparate frequencies, say blue and red, the κp cancels from the difference between two (4), and optical pressure is (at first order)

$$p_{\text{ops}} = \frac{2RT}{3A_2(\bar{\nu}_{\text{blue}}^2 - \bar{\nu}_{\text{red}}^2)} \left[\left(\frac{\Delta f}{\nu} \right)_{\text{red}} - \left(\frac{\Delta f}{\nu} \right)_{\text{blue}} \right]. \quad (5)$$

- The key attribute of (5) is that measuring the two frequencies in the quotient $\Delta f/\nu$ is independent of a pressure standard. Likewise, for helium, the dispersion polarizability A_2 is known from *ab initio* calculation, which is also independent of pressure.

- Consequently, (5) realizes p_{ops} without ancillary knowledge of pressure.

Apparatus

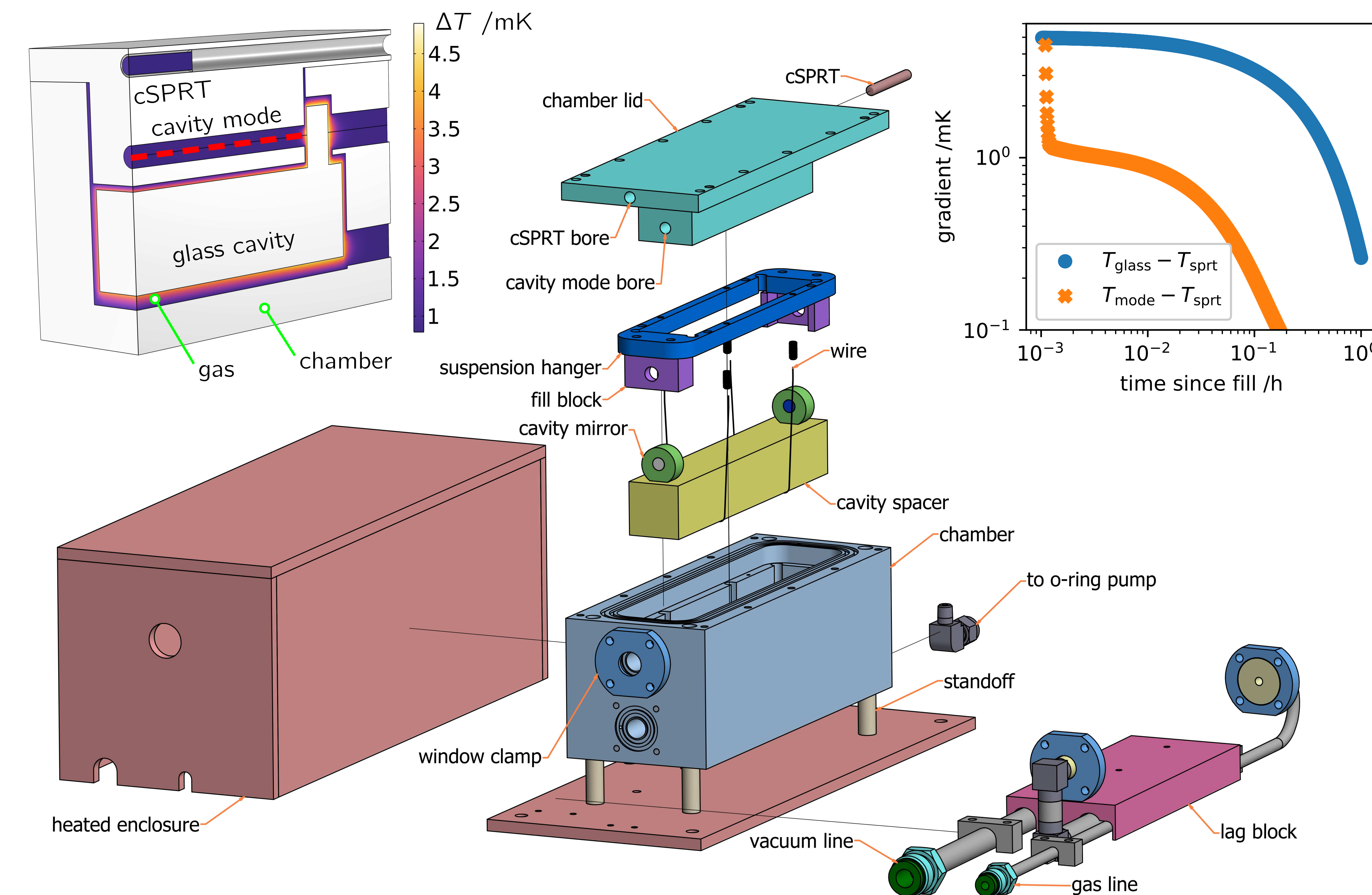


Fig. 1: Exploded view of the apparatus, plus some finite element results of the thermal response to a gas fill. Top left is a contour plot of thermal gradients in the argon volume, 360 s after a 0.1 MPa fill. Top right is gradients over time between the cavity mode T_{mode} or glass cavity T_{glass} , relative to the thermometer T_{sprt} .

Helium demonstration

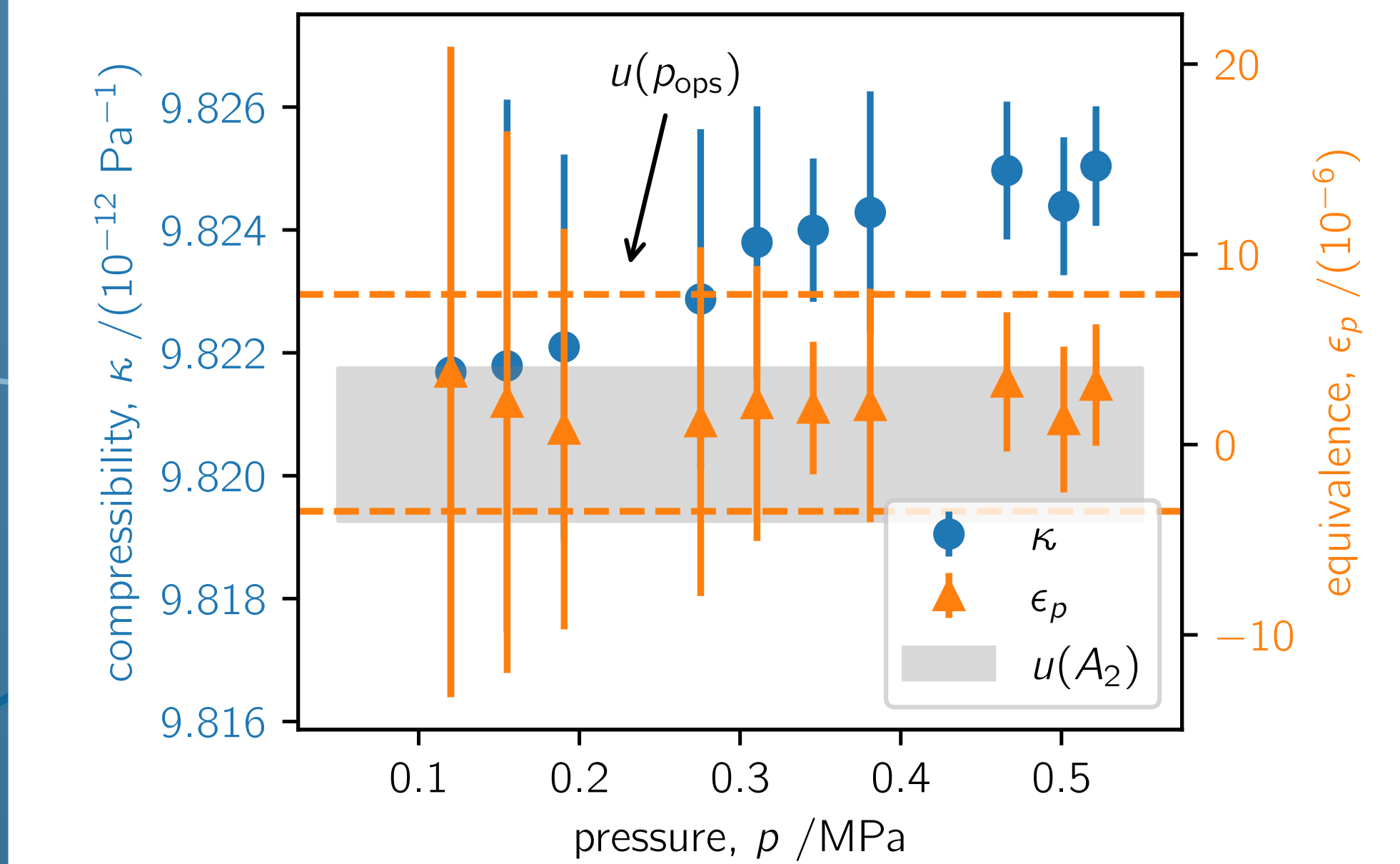


Fig. 2: Parameters κ and ϵ_p deduced by measurement of helium dispersion. The dashed lines show standard uncertainty in the experimentally realized optical pressure scale; the shaded area denotes the contributed uncertainty of dispersion theory.

Other gases

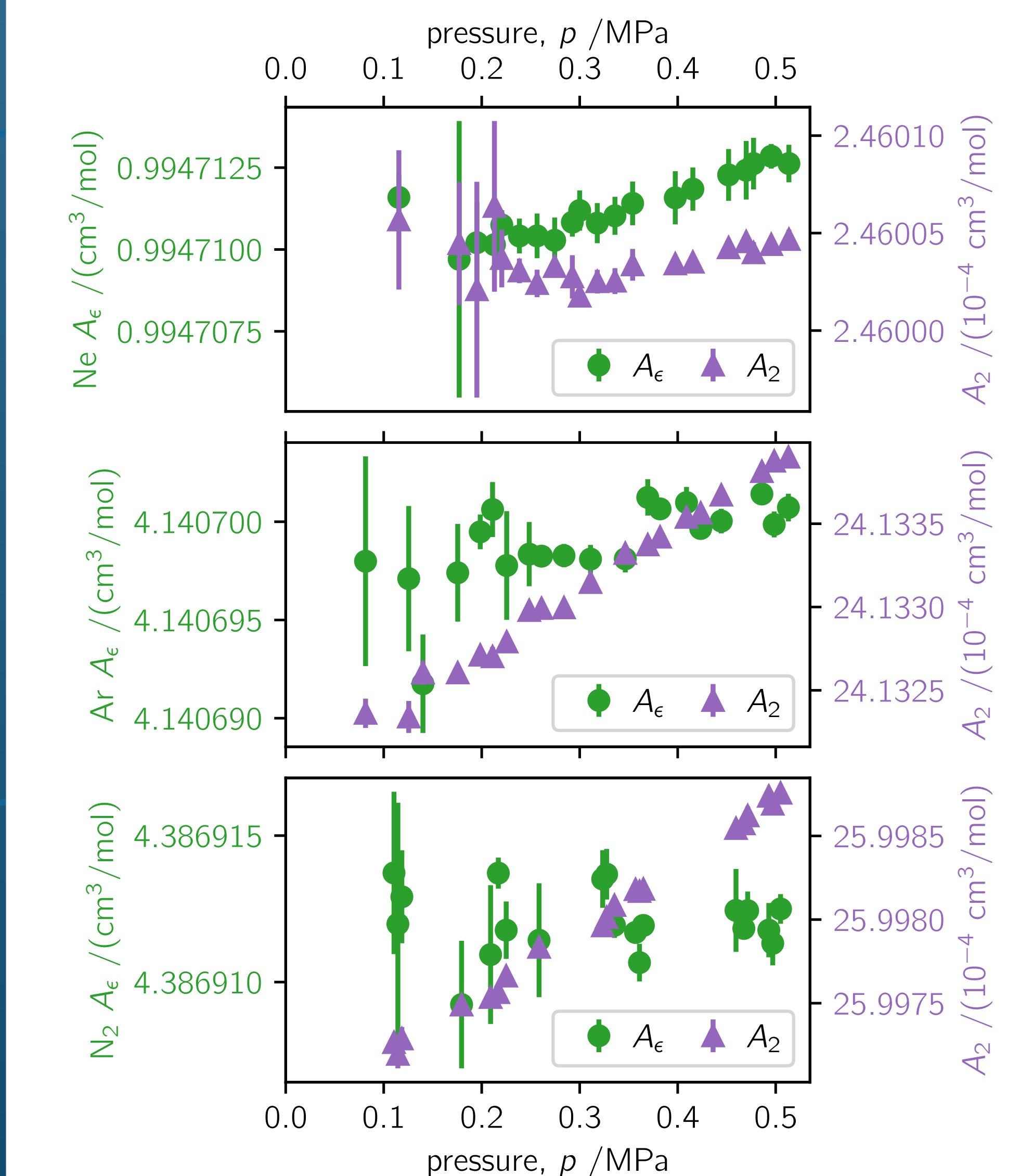


Fig. 3: Dispersion polarizability for the practical metrology gases. Errorbars span standard deviations on five repeats at each set pressure.