

Figure S1. NH(A-X,0-0) band spectrum.

Registered and calculated $N_2(C-B, 0-0)$ spectra, and their difference revealing the NH(A-X,0-0) band spectrum. Distance $x = 0$. The $N_2(C,0)$ rotational temperature, $T_{rot} = 1271$ K, was determined on the basis transition $N_2(C-B,0-2)$ spectrum as described in the paper. The registered and calculated spectra were fitted at 336.6–337 nm where the NH(A-X,0-0) intensity is low [1].

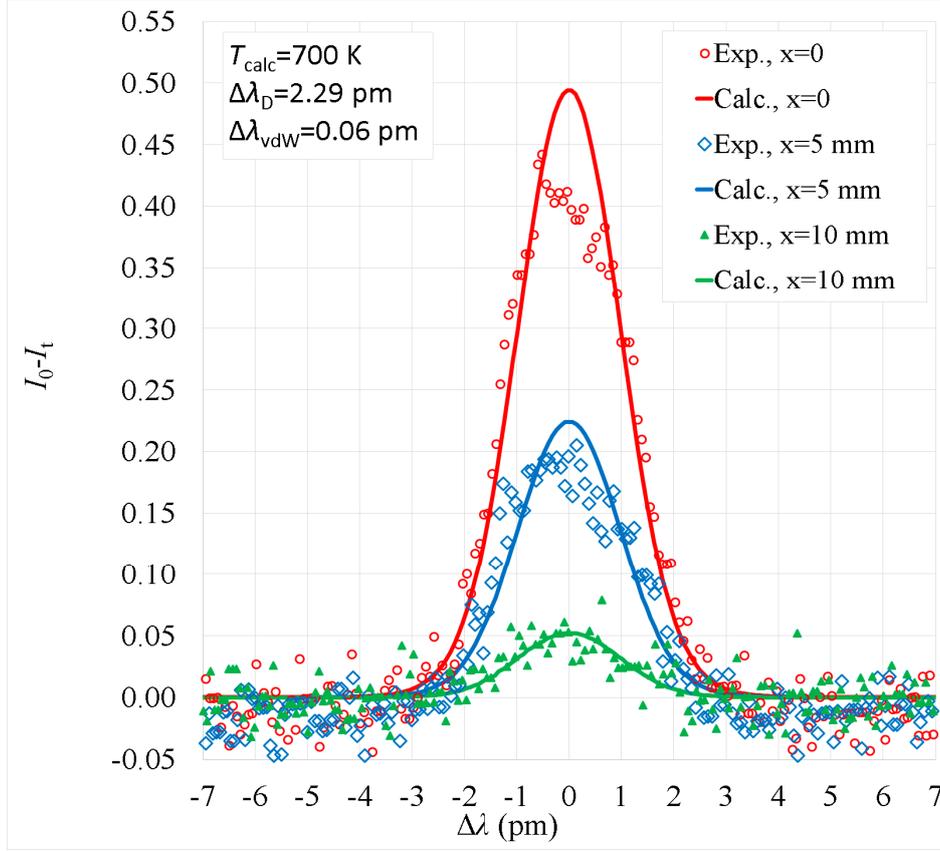


Figure S2. Temperature estimation from Ar ($1s_5 \rightarrow 2p_6$) line shape analysis. I_0 - the incident light intensity, I_t - the transmitted light intensity.

The absorption profile of the Ar spectral line $\lambda_0 = 763.5106$ nm (transition $1s_5 \rightarrow 2p_6$) [2], determined by TDLAS measurements, was fitted with a Voigt profile. Satisfactory fitting was found using the same temperature, 700 K, in the case of all experimental profiles. Two spectral line broadening mechanisms were considered: Doppler (Gaussian profile) and van der Waals (Lorentzian profile) broadening. The full width at half maximum (FWHM) of the Doppler broadening was calculated

as $\Delta\lambda_D = \sqrt{\frac{8 \cdot k_B \cdot T_g \cdot \ln(2)}{m_{Ar} \cdot c^2}} \cdot \lambda_0$, where k_B is Boltzmann's constant, T_g - the gas temperature, m_{Ar} - the mass of Ar atom, c - the speed of light. The FWHM of van der Waals broadening was calculated

as $\Delta\lambda_{vdW} = 8.18 \cdot 10^{-26} \cdot \lambda_0^2 \cdot (\alpha \cdot \langle \bar{R}^2 \rangle)^{2/5} \cdot \left(\frac{T_g}{\mu}\right)^{3/10} \cdot N$ [3]. Here, λ_0 is in nm, α - the atomic polarizability of the neutral perturber ($16.54 \cdot 10^{-25}$ cm³), T_g is in K, N - the concentration of atoms in cm⁻³, μ - reduced mass of the colliding atoms in AMU (for Ar $\mu \approx 20$). $\langle \bar{R}^2 \rangle = \langle \bar{R}_U^2 \rangle - \langle \bar{R}_L^2 \rangle$, with $\langle \bar{R}_U^2 \rangle$ and $\langle \bar{R}_L^2 \rangle$ been the mean square radiuses (in Bohr radius units) of the atom in upper and lower levels and $\langle \bar{R}_{U|L}^2 \rangle = \frac{1}{2} \cdot n^{*2} [5n^{*2} + 1 - 3l_{U|L}(l_{U|L} + 1)]$. In this formula $l_U = 1$ and $l_L = 0$ are the orbital angular momentum quantum numbers and $n^{*2} = \frac{E_H^i}{E_{Ar}^i - E_{2p_6}}$ is the effective quantum number

with ionization potentials $E_H^i = 13.60$ eV and $E_{Ar}^i = 15.76$ eV of hydrogen and argon atoms and $E_{2p_6} = 13.17$ eV is the energy of Ar($2p_6$) atom [2].

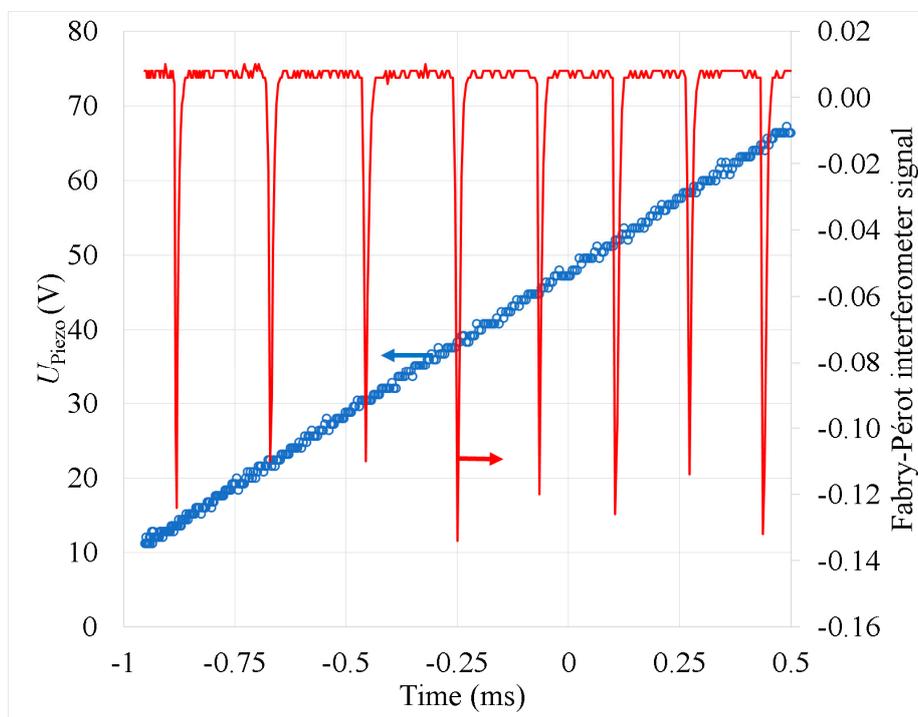


Figure S3. TDLAS laser stability on the basis of Fabry-Pérot interferometer signal.

Example of Fabry-Pérot interferometer signal in response to the linear increase in the voltage on the piezoelectric element (U_{Piezo}) that changed the laser resonator length. The dependence of the Fabry-Pérot interferometer signal on time was used to determine the laser wavelength change and check the laser operation stability.

Reference

1. Sekiya, H.; Nishiyama, N.; Tsuji, M.; Nishimura, Y. Nascent Vibrational and Rotational Distributions of NH(A) in the Dissociative Excitation of NH₃ by Ar(3P₂,0) at Thermal Energy. *J. Chem. Phys.* **1987**, *86*, 163–169.
2. Kramida, A.; Ralchenko, Y.; Reader, J.; NIST ASD Team NIST Atomic Spectra Database Available online: <https://physics.nist.gov/asd>.
3. Muñoz, J.; Dimitrijević, M.S.; Yubero, C.; Calzada, M.D. Using the van Der Waals Broadening of Spectral Atomic Lines to Measure the Gas Temperature of an Argon-Helium Microwave Plasma at Atmospheric Pressure. *Spectrochim. Acta - Part B At. Spectrosc.* **2009**, *64*, 167–172, doi:10.1016/j.sab.2008.11.006.