

Invited talk

# High-accuracy molecular spectroscopy exploiting resonant frequencies of an optical cavity

**Lisak D.<sup>†</sup>***Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń,  
Grudziądzka 5, 87-100 Toruń, Poland*<sup>†</sup>dlsak@umk.pl

Laser spectroscopy applications for quantitatively detecting gas amount and composition are based on accurate measurements of reference line intensities and collisional line shapes. Exceptionally high accuracies of such data are required in atmospheric research focused on greenhouse gases where line intensities must be known at permille-level uncertainties. Similar or even lower uncertainties are needed for the realization of optical gas amount, concentration, and temperature standards, which, after the recent SI redefinition, allows greater flexibility in linking fundamental constants to measurable quantities.

We demonstrate low-uncertainty line intensities and line shapes of carbon monoxide<sup>1,2,3,4</sup> and hydrogen molecules<sup>3</sup> obtained through a combination of cavity-enhanced absorption and dispersion spectroscopies, interlaboratory comparison of independent measurements, and *ab initio* calculations. We also show that per mille uncertainties of line intensity for hydrogen molecules<sup>4</sup> require an advanced collisional line shape model<sup>5</sup> that goes beyond the standard description used in spectroscopic databases. Our experimental data were obtained using cavity mode-dispersion spectroscopy (CMDs)<sup>6</sup> and recently developed heterodyne cavity ring-down spectroscopy (HCRDS)<sup>3</sup> that exploit optical cavity resonant frequencies and enable high-resolution gas absorption and dispersion measurement with spectra fully linked to the primary frequency standard.

We also present the first primary spectroscopic thermometry leveraging optical cavity resonance frequencies and *ab initio* molecular line intensities<sup>7</sup>. Using CO rovibrational transitions, our frequency-based approach, achieving temperature uncertainty of 82 parts per million, is much more accurate than any reported spectroscopic thermometry at pressures above 1 kPa and applies to a tenfold broader pressure range. In particular, it enables fully optical, molecule-selective primary amount-of-substance measurements without contact sensors, achieving sub-permille uncertainty in gas concentration and pressure.

The research was supported by the state budget of Poland, allocated by the Minister of Education and Science under the "Polska Metrologia II" program, project no. PM-II/SP/0011/2024/02 and the European Partnership on Metrology project "22IEM03 PriSpecTemp".

<sup>1</sup>K. Bielska, *et al.*, *Phys. Rev. Lett.* **129**, 043002 (2022).<sup>2</sup>A. A. Balashov, *et al.*, *J. Chem. Phys.* **158**, 234306 (2023).<sup>3</sup>J. T. Hodges, *et al.*, *Metrologia* **62**, 08006 (2025).<sup>4</sup>A. Cygan *et al.*, *Sci. Adv.* **11**, eadp8556 (2025).<sup>5</sup>R. Ciuryło, *et al.*, *Phys. Rev. A* **65**, 012502 (2002).<sup>6</sup>A. Cygan *et al.*, *Opt. Express* **23**, 14472 (2015).<sup>7</sup>D. Lisak *et al.*, arXiv:2502.17660 [physics.optics] (2025).