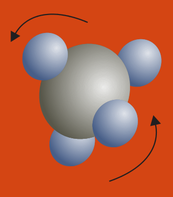
Reference data for optical spectroscopy of small molecules

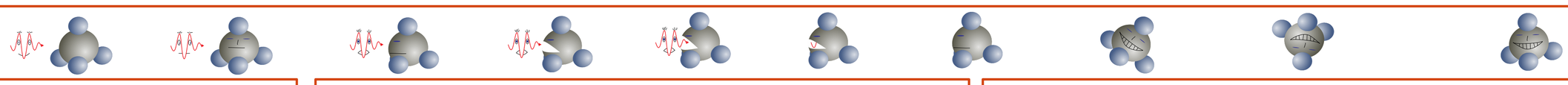


Abstract

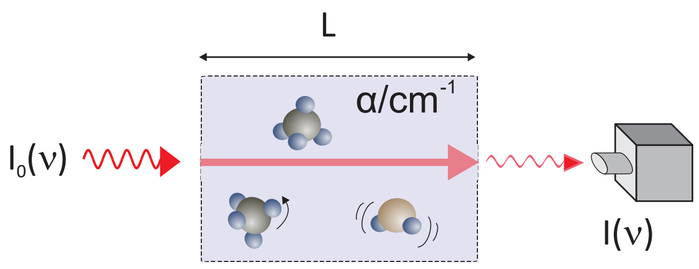
In our laboratory, we study the interaction of light with **small molecules** (e.g., ammonia or NOx radicals). These particles often play a crucial role in everyday physical and chemical processes on both **terrestrial** and **cosmic** scales. One example is the characterization of exoplanets based on detecting such molecules in their atmospheres.

A thorough understanding of **the optical spectra** of these molecules and their interactions is necessary for correct and effective analysis of absorption signals. The best way to obtain this data is through sensitive laboratory measurements, where reference spectra can be collected under known experimental conditions (as opposed to studied objects, where these data must be inferred from measurements). Our group focuses both on developing new optical detectors (e.g., **CEAS** and **CRDS**) and processing spectroscopic data to create reference databases. Our most significant achievement in this field is our participation in developing a new version of the **HITRAN** database, the most renowned molecular reference spectroscopy database

Methods



Absorption spectroscopy



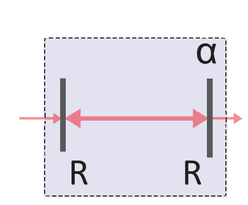
$$\alpha = -\frac{1}{L}\ln\{\frac{I}{I_0}\} \leftarrow I = I_0 \exp[-\alpha L]$$

$$\delta\alpha = -\frac{1}{L}\frac{\delta I}{I_0}$$

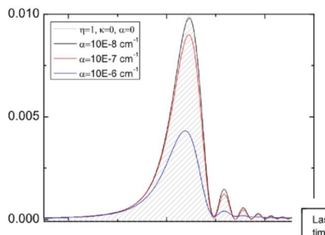
Longer the path, **better**!

(more sensitivity)

Trapping the light

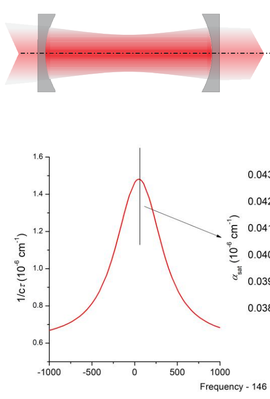


~L/(1-R)



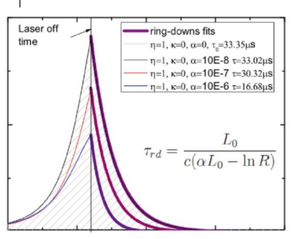
Cavity
Enhanced
Aabsorption
Spectroscopy

Relative measurement of α



Cavity
Ring
Down
Spectroscopy

Absolute measurement of α

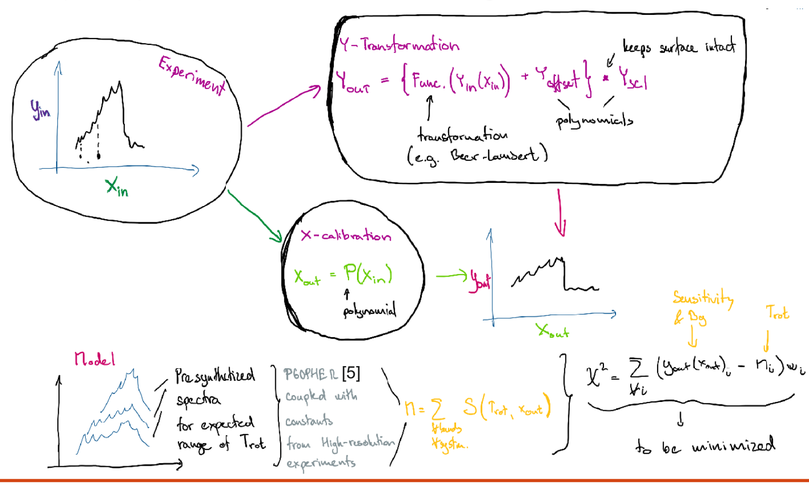


Combining optical cavity and frequency-referenced light source an unprecedented

Accuracy & Sensitivity could be achieved [2].

Radiative transfer (model)

The modeling of ro-vibrational transitions is a key ability to extract the information from the spectra. In our recent study [1] we were able to present the first application of the N2-HIR ro-vibrational model for the metrology of the atmospheric-pressure dielectric-barrier discharge.



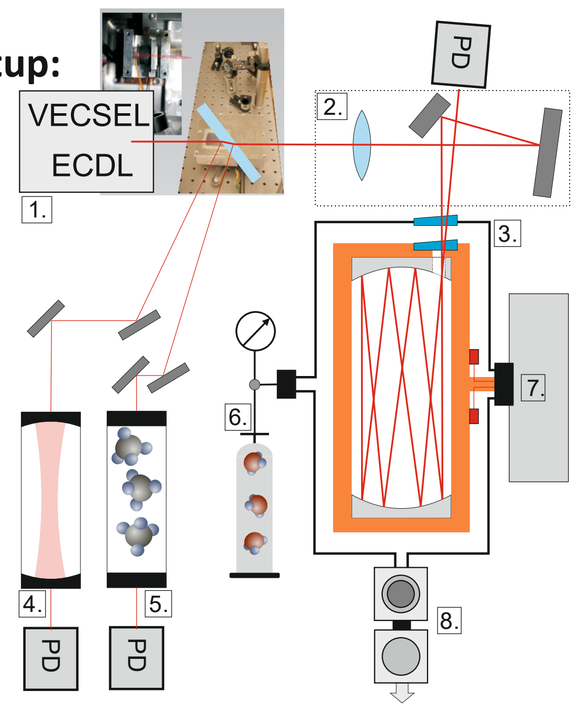
Low Temperature Spectroscopy [3].

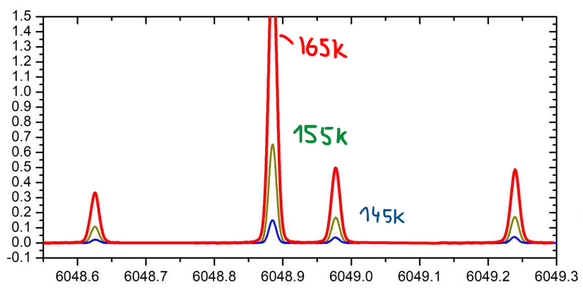
Measurement of molecular absorption as a function of temperature (determination of vapour pressures, line intensities, nuclear spin populations)

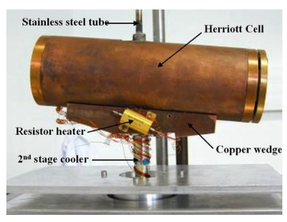
Experimental setup:

(1) Tunable Laser
(2) Cell matching optics
(3) Herriott cell system
(4) Fabry-Perot etalon
(5) Reference CH4 cell
(6) Gas control
(7) Temperature control
(8) Pumping

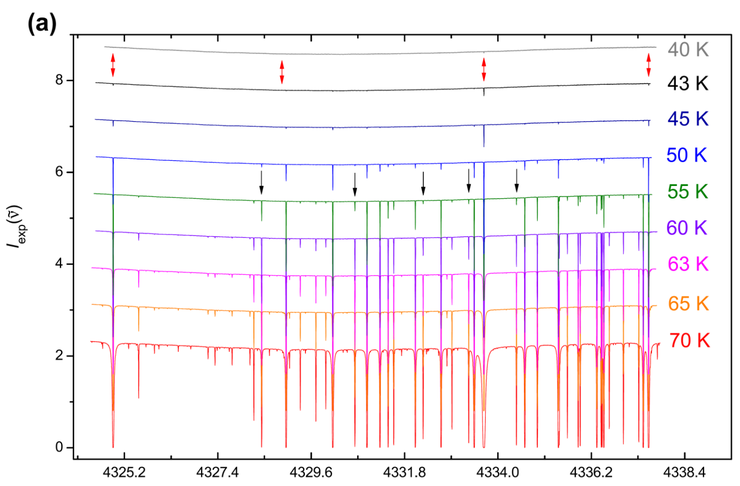
Herriot cell:
698 cm path length
absolute precision
0.5K from 10K to 30K
0.25K from 30K to 60K
0.15K from 60K to 300K
relative stability
< 0.001K
uniformity
< 0.02K

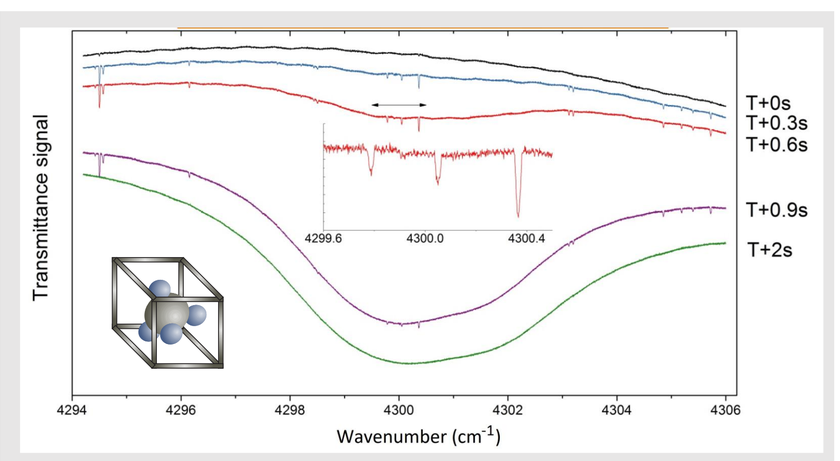






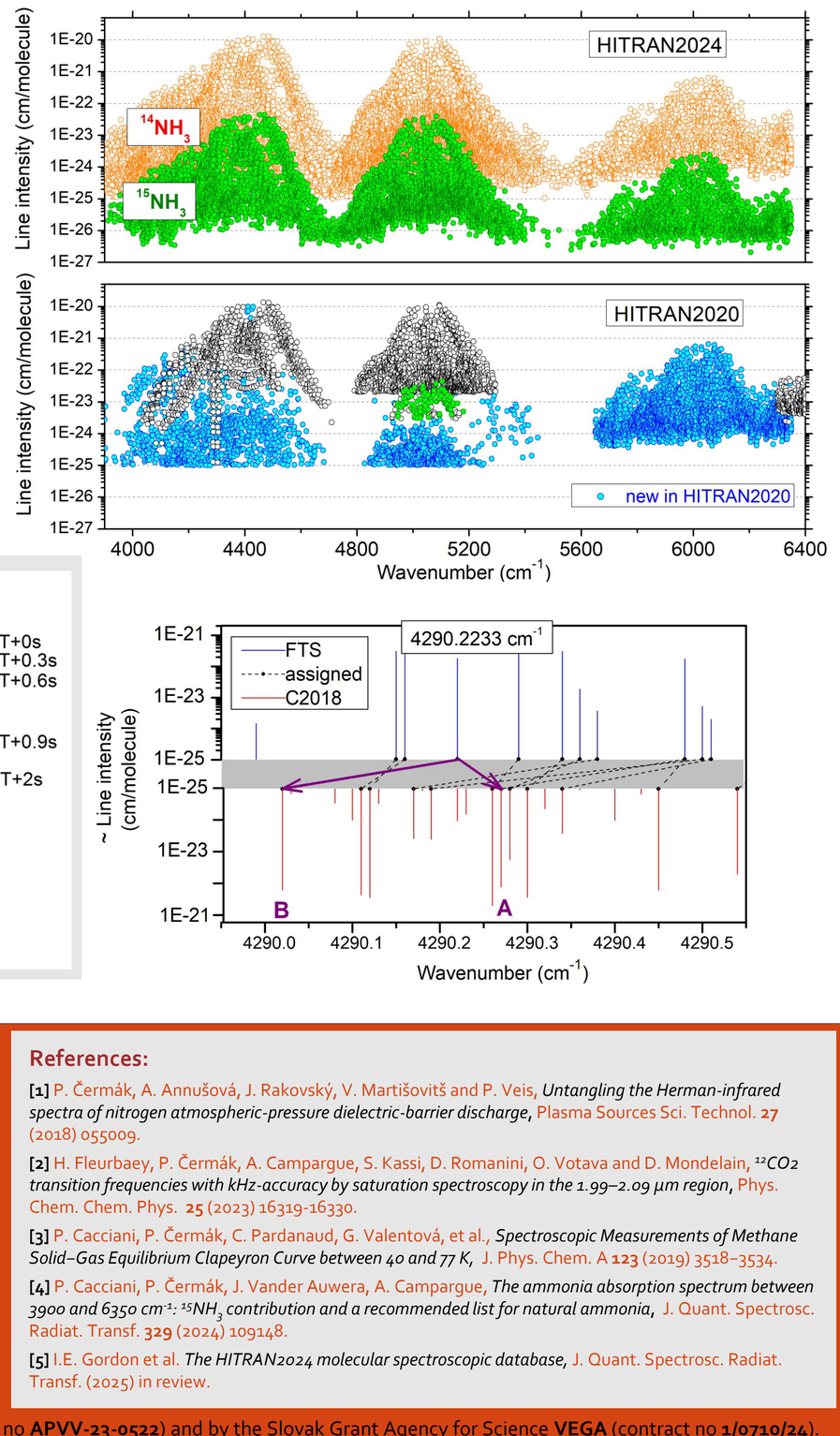
Ongoing & Future Work





HITRAN2024 [4, 5].

Measurement of line position, intensity and quantum assignment for NH_3



FAKULTA MATEMATIKY, FYZIKY A INFORMATIKY
Univerzita Komenského v Bratislave

Peter Čermák, Filip Pastierovič
Comenius University Bratislava, Slovakia

MATFYZ CONNECTIONS

References:

[1] P. Čermák, A. Annušová, J. Rakovský, V. Martišovitš and P. Veis, *Untangling the Herman-infrared spectra of nitrogen atmospheric-pressure dielectric-barrier discharge*, Plasma Sources Sci. Technol. **27** (2018) 055009.

[2] H. Fleurbaey, P. Čermák, A. Campargue, S. Kassi, D. Romanini, O. Votava and D. Mondelain, *$^{12}CO_2$ transition frequencies with kHz-accuracy by saturation spectroscopy in the 1.99–2.09 μm region*, Phys. Chem. Chem. Phys. **25** (2023) 16319-16330.

[3] P. Cacciani, P. Čermák, C. Pardanaud, G. Valentová, et al., *Spectroscopic Measurements of Methane Solid–Gas Equilibrium Clapeyron Curve between 40 and 77 K*, J. Phys. Chem. A **123** (2019) 3518–3534.

[4] P. Cacciani, P. Čermák, J. Vander Auwera, A. Campargue, *The ammonia absorption spectrum between 3900 and 6350 cm^{-1}: $^{15}NH_3$ contribution and a recommended list for natural ammonia*, J. Quant. Spectrosc. Radiat. Transf. **329** (2024) 109148.

[5] I.E. Gordon et al. *The HITRAN2024 molecular spectroscopic database*, J. Quant. Spectrosc. Radiat. Transf. (2025) in review.

This research was supported by the Slovak Research and Development Agency (contract no **APVV-23-0522**) and by the Slovak Grant Agency for Science **VEGA** (contract no **1/0710/24**).