

Quantitative measurement of OH radical using Faraday rotation spectroscopy at 2.8 μm

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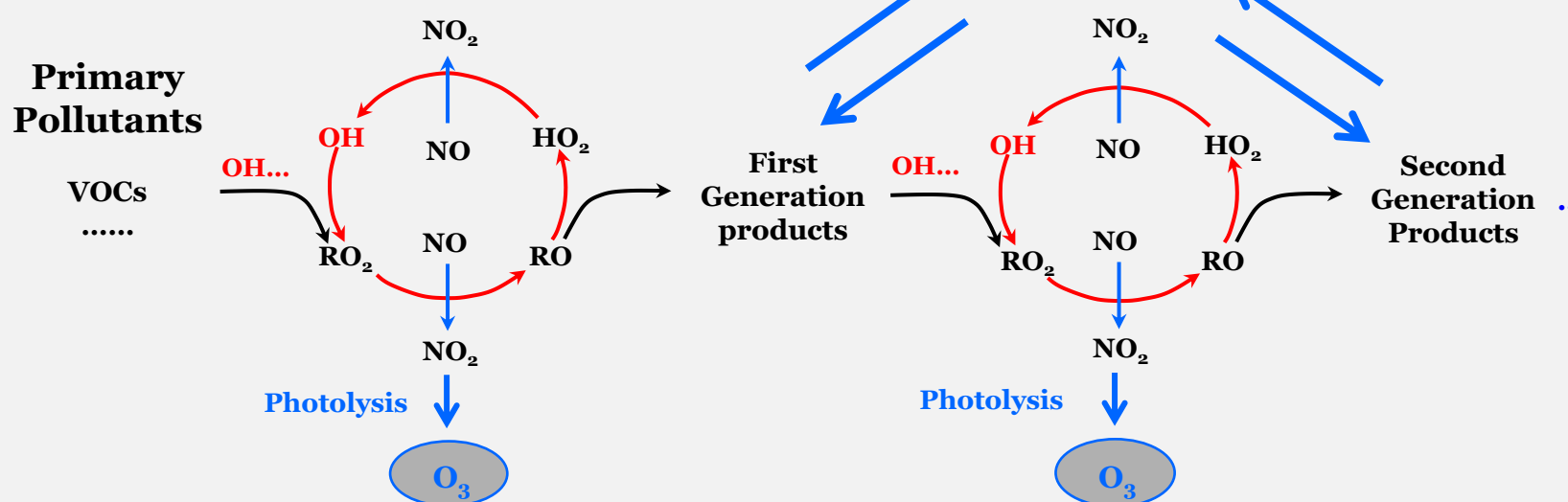
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Motivation for OH detection

OH plays a crucial role in the degradation of trace gases and pollutants in the troposphere and in controlling the atmospheric oxidation capacity.



The concentration of OH is a measure of atmospheric self-cleansing and can be enhanced by its regeneration in the oxidation chain of reaction products.

The budget is generally controlled by *in situ* chemistry, which makes OH an ideal target for the validation of atmospheric models through the comparison between observations and model predications.

Total OH reactivity (k_{OH}')

k_{OH}' is equal to the reciprocal of the atmospheric lifetime of OH (τ_{OH}) and is an important parameter for quantitative assessment of the atmospheric oxidation capacity. It is defined as the total pseudo-first-order loss rate of OH in ambient air caused by the reactions of OH with most pollutants and greenhouse gases, such as volatile organic compounds (VOCs), CO, NO_x ($= \text{NO} + \text{NO}_2$), CH_4 , etc..

$$k_{\text{OH}}' = \sum k_{\text{OH}+X_i} [X_i] = \tau_{\text{OH}}^{-1}$$

where X_i represents the reactive species with concentration $[X_i]$. $k_{\text{OH}+X_i}$ is the reaction rate coefficient of OH with each species.

Due to its high reactivity and short lifetime, the production (P_{OH}) and sink ($k_{\text{OH}}' [\text{OH}]$) of atmospheric OH radicals can be described by steady-state equation:

$$\frac{d[\text{OH}]}{dt} = P_{\text{OH}} - k_{\text{OH}}' [\text{OH}] = 0$$

Measurement of k_{OH}' in combination with OH concentration ($[\text{OH}]$) provides insight into OH production and loss processes and is a powerful test of our understanding of atmospheric oxidation chemistry.

The challenges for OH measurement

Because of its very short lifetime ($\tau_{\text{OH}} \sim 0.01\text{--}1\text{ s}$) and very low concentration in the atmosphere ($[\text{OH}] \sim 10^6\text{--}10^7$ molecule/ cm^3), interference-free high sensitivity *in situ* OH monitoring by laser spectroscopy represents a real challenge. To date, only two spectroscopic methods, fluorescence assay by gas expansion (FAGE) at low pressure and long-path differential optical absorption spectroscopy (DOAS), have been successfully employed for tropospheric OH measurement with detection limits of $\sim 10^5\text{--}10^6$ radicals/ cm^3 .

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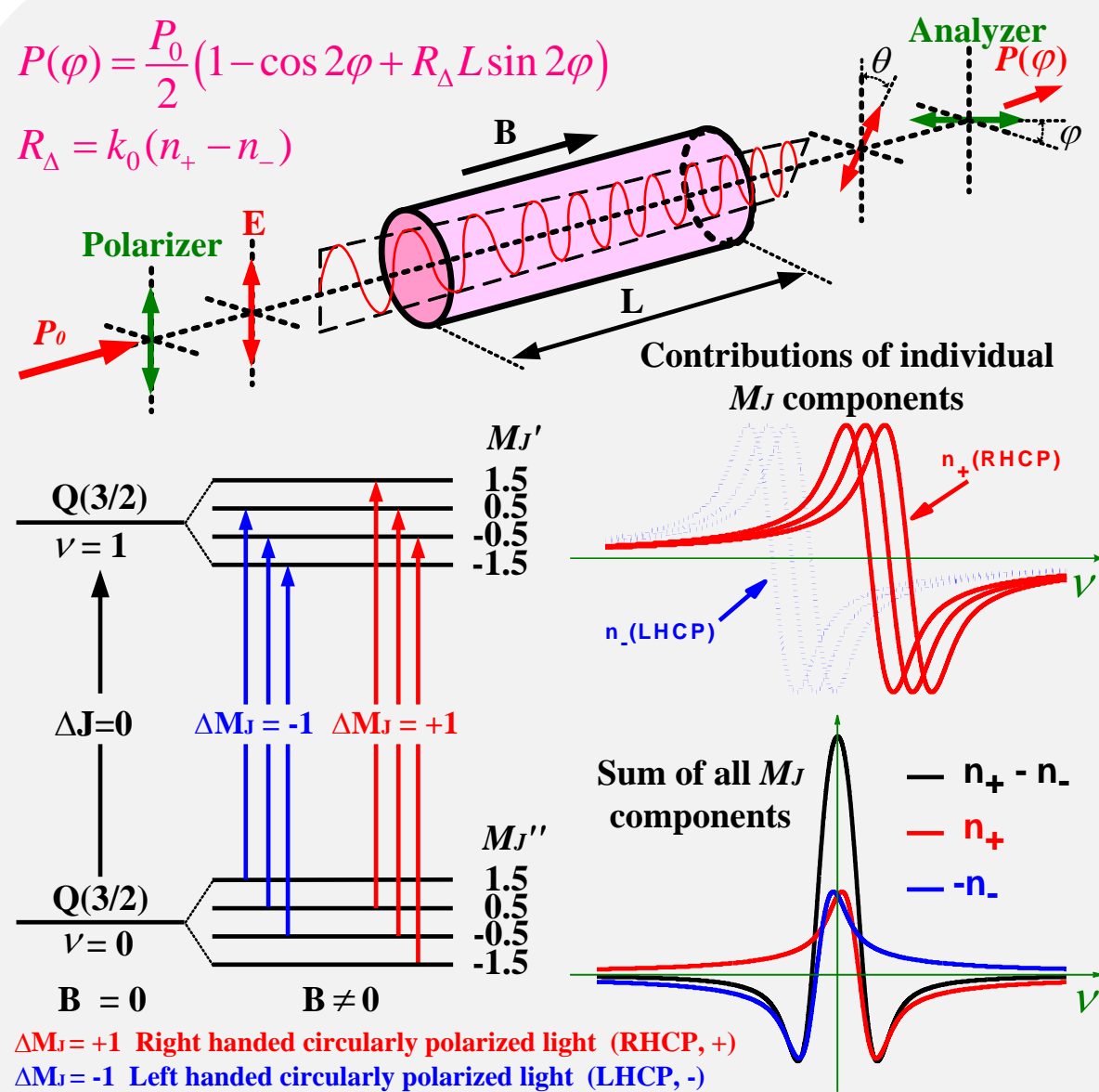
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Faraday rotation spectroscopy (FRS)



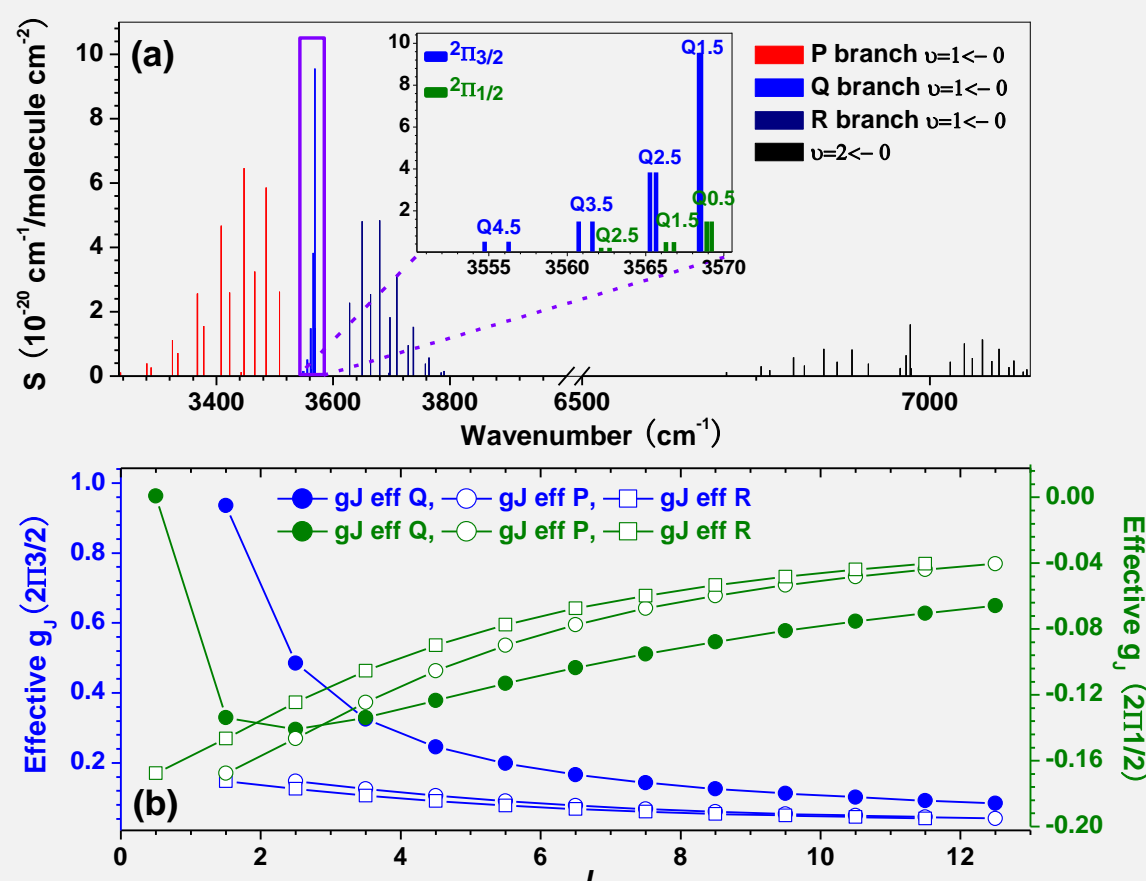
- (1) The FRS relies on the particular magneto-optic effect observed for paramagnetic species, diamagnetic species do not produce any significant Faraday rotation effect.
- (2) The use of two nearly crossed polarizers with high extinction ratio provides a significant reduction of the laser source noise.
- (3) Zeeman splitting of the molecular absorption line (and thus the magnetic circular birefringence) is modulated. This provides an “internal modulation” of the sample, thus the external noise like interference fringes can be easily suppressed.

FRS is suitable for high sensitive measurement of reactive species.

The FRS signal depends on :

- ✓ **Molecular line strength**
- ✓ **Optical path length**
- ✓ **g -factor and magnetic field strength**
- ✓ **Molecule concentration**

Selection of optimum transition of OH radical



The highest absorption line intensity and the largest g_J factor (rotational gyromagnetic ratio) make the Q(1.5) double lines at $\sim 3568 \text{ cm}^{-1}$ clearly the best choice for FRS detection in the infrared region.

□ **Q(1.5) double lines @ $\sim 3568 \text{ cm}^{-1}$:**

- ✓ the strongest absorption in the infrared region
- ✓ large g_J value allowing use of small magnetic field

□ **Q branch:**

- ✓ the same magnetic modulation sensitivity
- ✓ the most efficient summation of all the transitions

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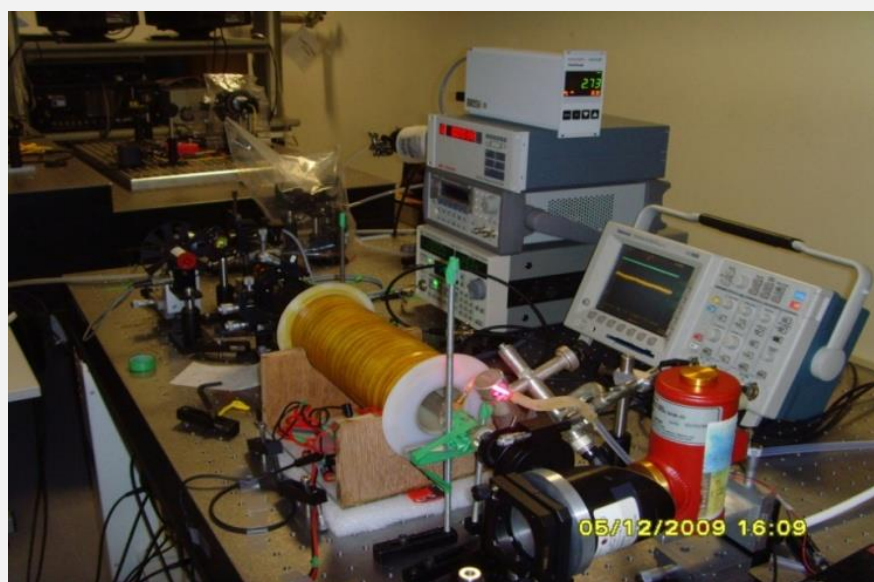
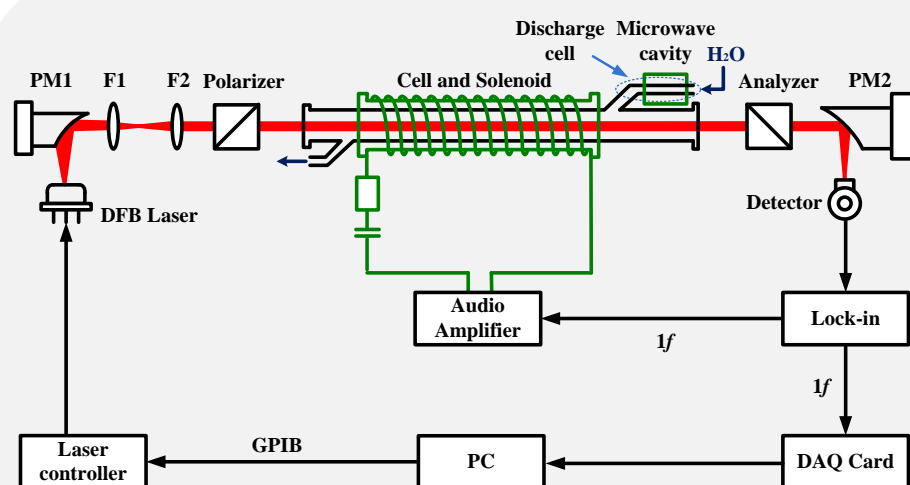
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FRS set up with AC field



Prototype instrument for self-calibrated OH measurement

OH radical was produced by a 2.45 GHz micro-wave (MW) discharge of H₂O.

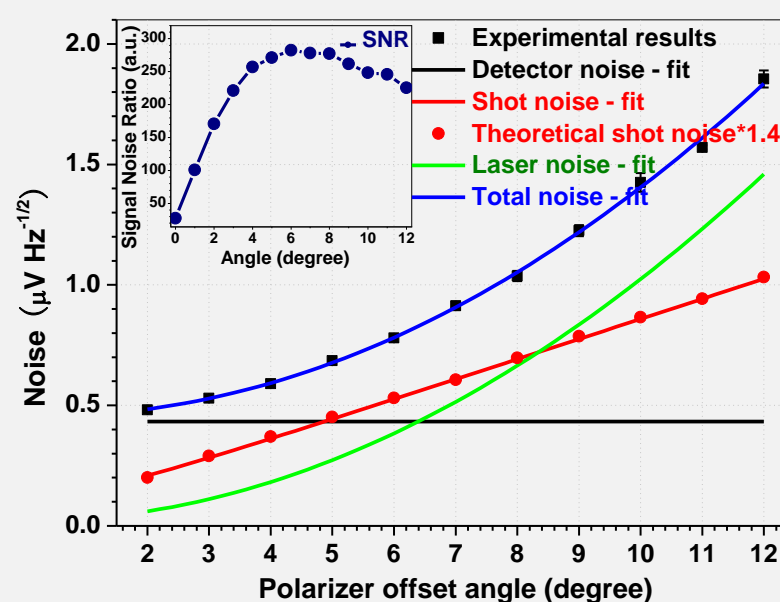
Room temperature DFB diode laser at 2.8 μm

➤ Single-mode tuning range : $\sim 5 \text{ cm}^{-1}$

➤ CW laser emission power : $\sim 2 \text{ mW}$

Polarizers : high extinction ratio of $\xi < 5 \times 10^{-6}$

Solenoid : 25 cm long, operating in AC mode at a resonant frequency of 1.302 kHz, with a magnetic field of $B \sim 95 \text{ Gauss}_{\text{rms}} / A_{\text{rms}}$



Optimization of the analyzer rotation angle

Maximum SNR @ $\varphi = 6^\circ$, *shot noise predominate.*

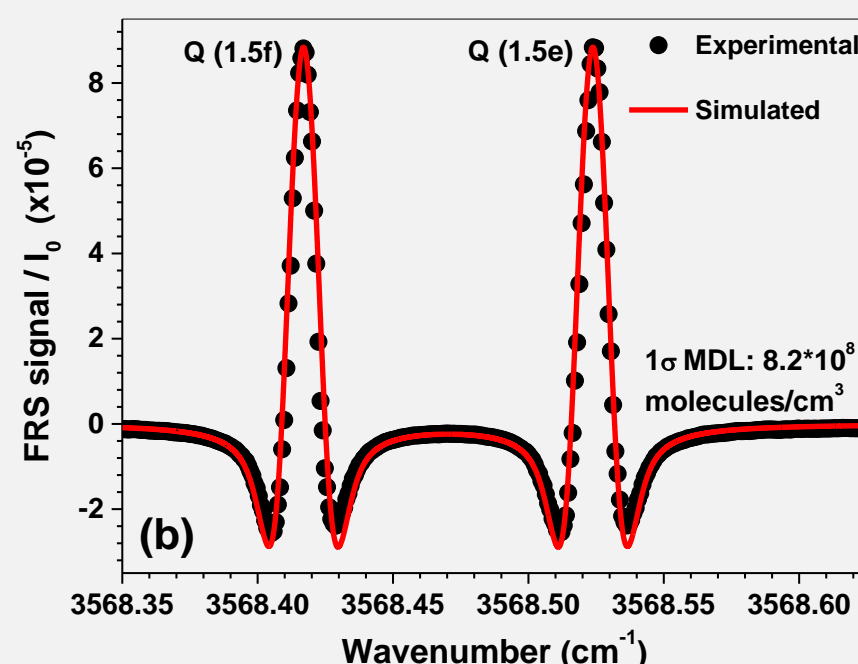
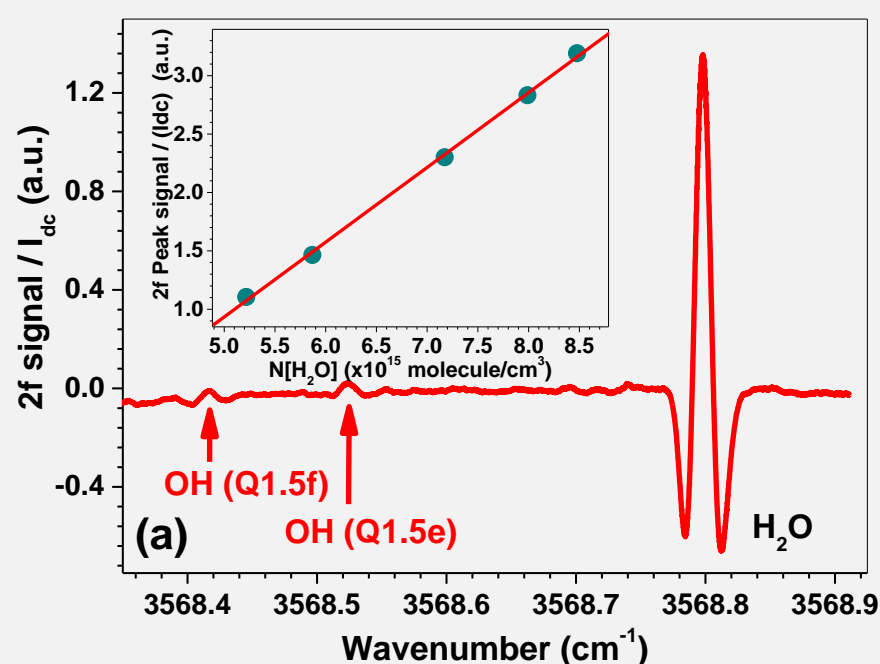
Zhao, W. X., et al. (2011). "Sensitive and selective detection of OH radicals using Faraday rotation spectroscopy at 2.8 μm ." *Optics Express* 19(3): 2493-2501.

Zhao, W., et al. (2012). "High sensitivity Faraday rotation spectrometer for hydroxyl radical detection at 2.8 μm ." *Applied Physics B* 109(3): 511-519.

FRS signal (comparison with WMS signal)

WMS 2f, L=25cm, $\alpha_{\text{min}} \sim 2 \times 10^{-6} \text{ cm}^{-1}$

FRS, L=25cm, $\alpha_{\text{min}} \sim 7 \times 10^{-9} \text{ cm}^{-1}$



The prototype instrument achieves a 1 σ detection limit of $8.2 \times 10^8 \text{ molecules/cm}^3$. (25 cm long optical pathlength, lock-in time constant of 100 ms)

More than two orders improved in sensitivity compared with WMS!

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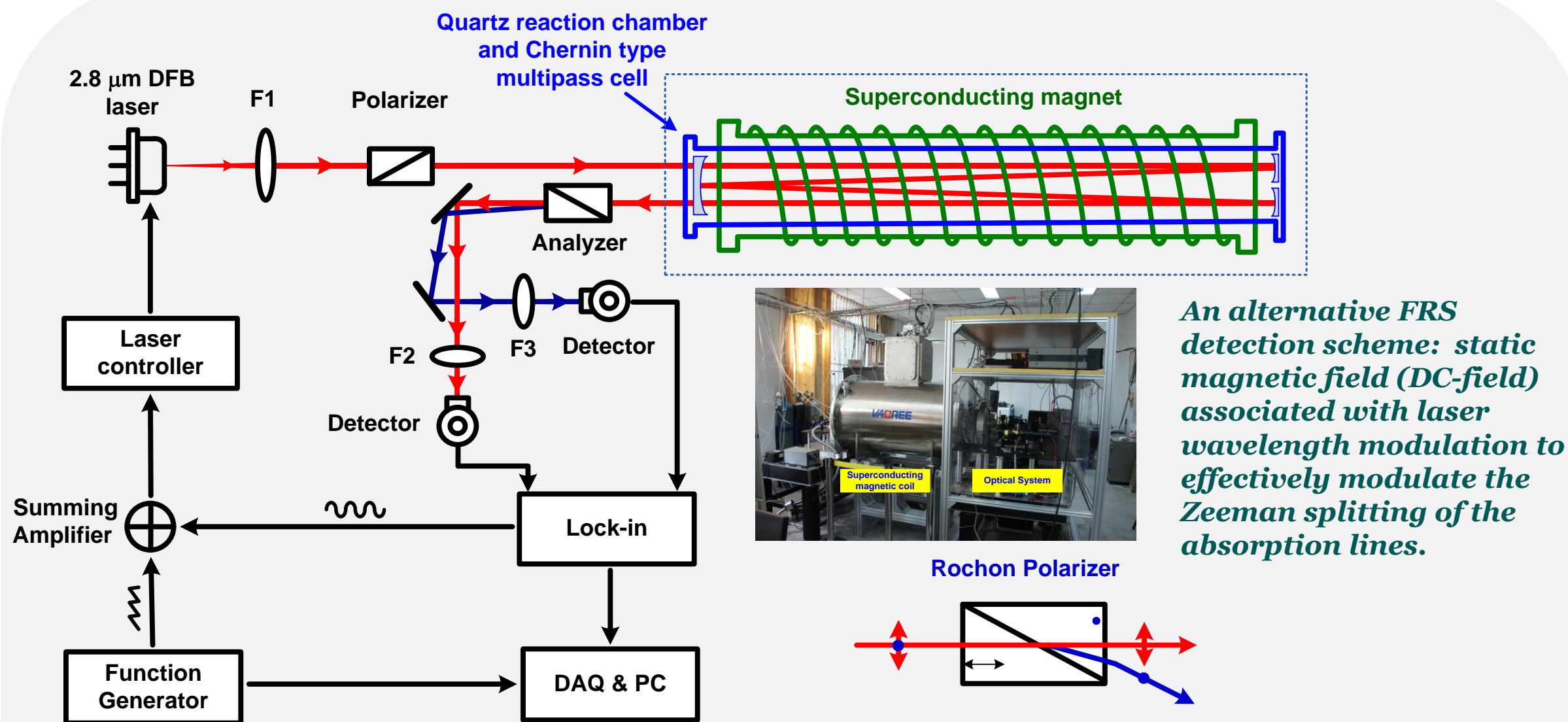
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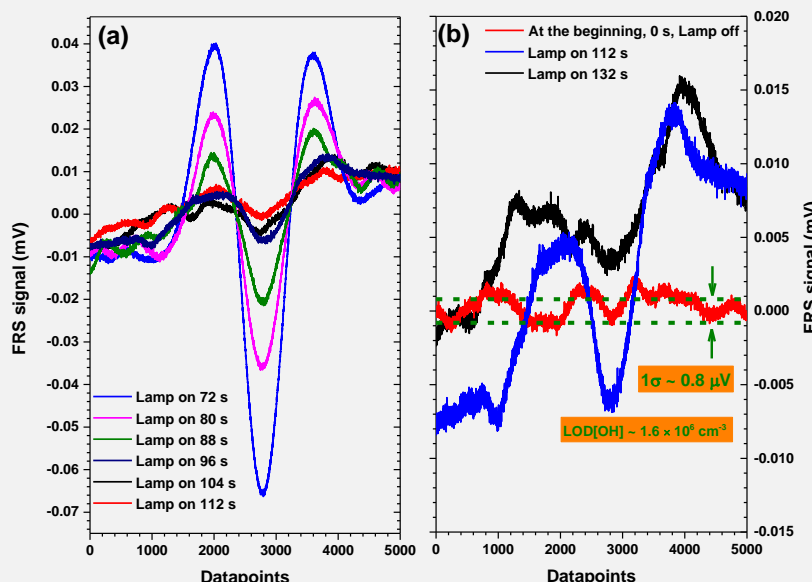
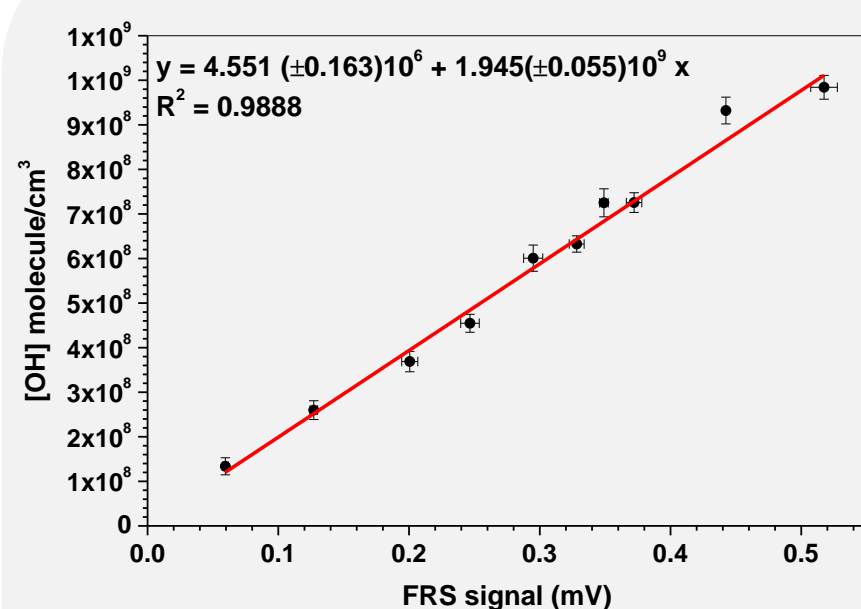
Superconducting-magnet-based Faraday rotation spectrometer



For FRS chamber application, a large-diameter magnet is required. The detection sensitivity of FRS can be further improved by implementing long absorption path lengths with multipass cells. The commonly used solenoid coil wrapped by enamel-copper wire can not meet the requirement due to the high winding resistance.

We report the first development of a superconducting-magnet-based Faraday rotation spectrometer operating at 2.8 μm for real time in situ measurement of OH in a chamber.

FRS signals during the O₃ photolysis in the chamber



With the use of a multipass enhanced FRS, a detection limit of $1.6 \times 10^6 \text{ OH}/\text{cm}^3$ (1σ , 4s) was achieved with an absorption path length of 108 m.

The developed FRS system provided a unique, self-calibrated analytical instrument for in situ direct measurement of chamber OH concentration.

Zhao, W. X., et al. (2018). "Superconducting-magnet-based Faraday rotation spectrometer for real time in situ measurement of OH radicals at $10^6 \text{ molecule}/\text{cm}^3$ level in an atmospheric simulation chamber." *Analytical Chemistry* 90(6): 3958-3964.

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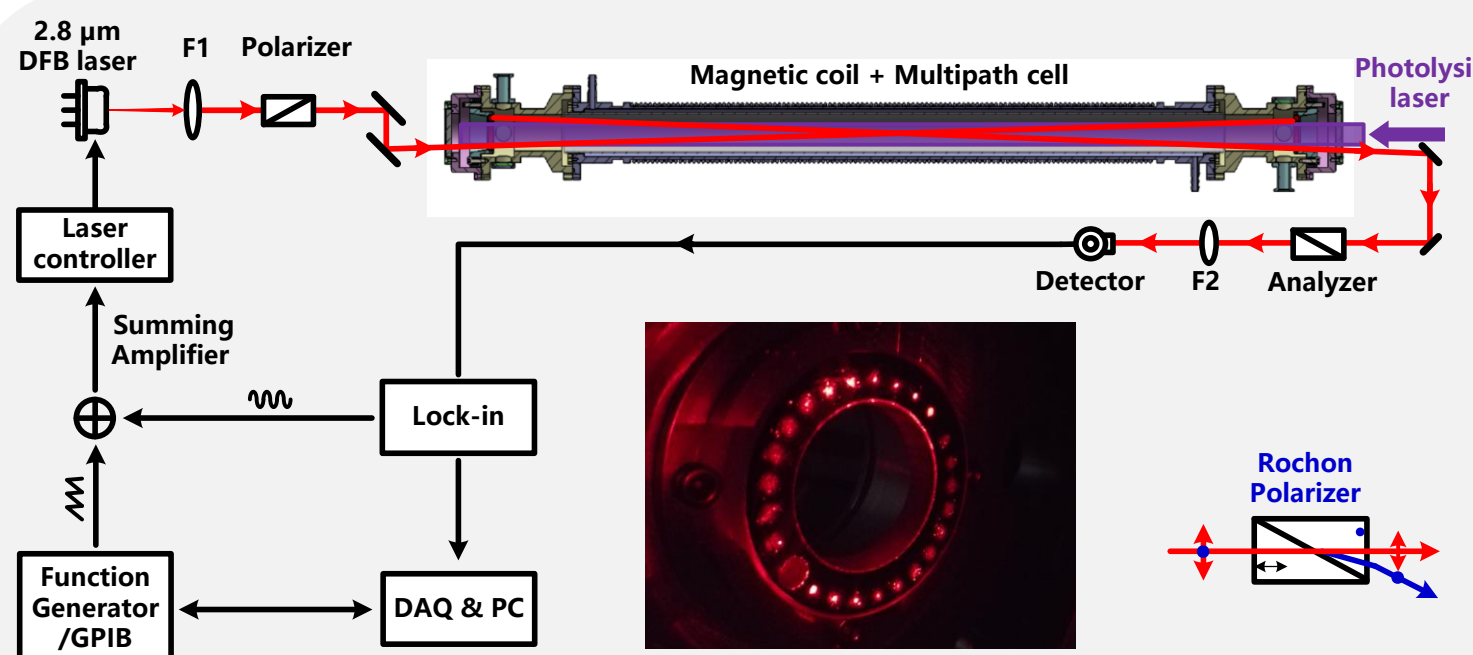
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Time-resolved laser-flash photolysis Faraday rotation spectrometer

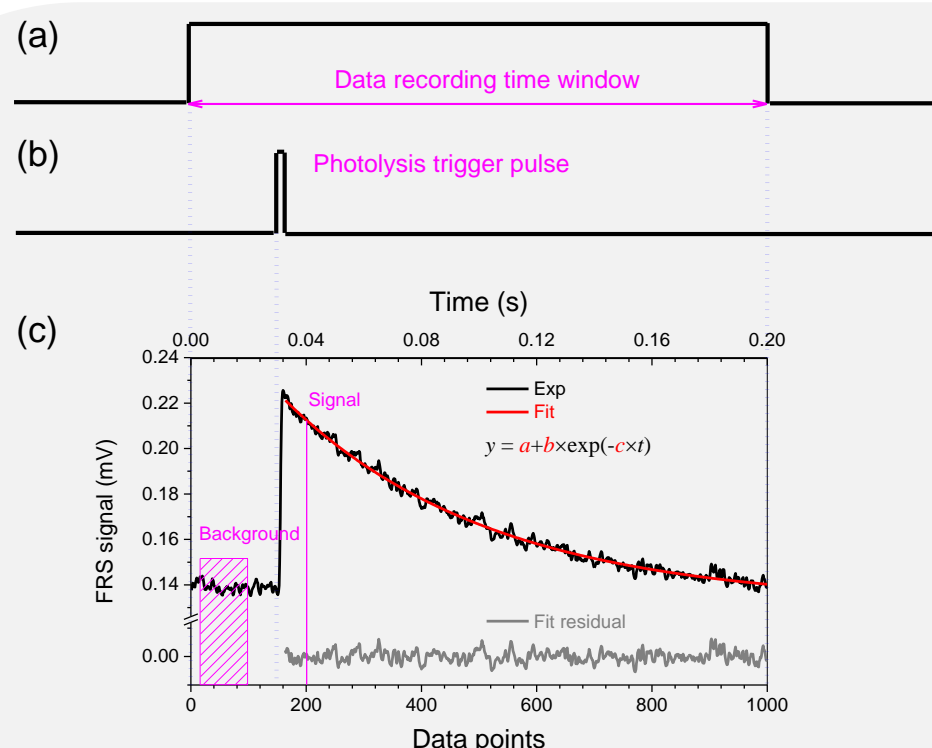


A new instrument that combines laser-flash photolysis with mid-infrared Faraday rotation spectroscopy (LFP-FRS) for real-time in-situ measurement of k_{OH} and free radical kinetics studies.

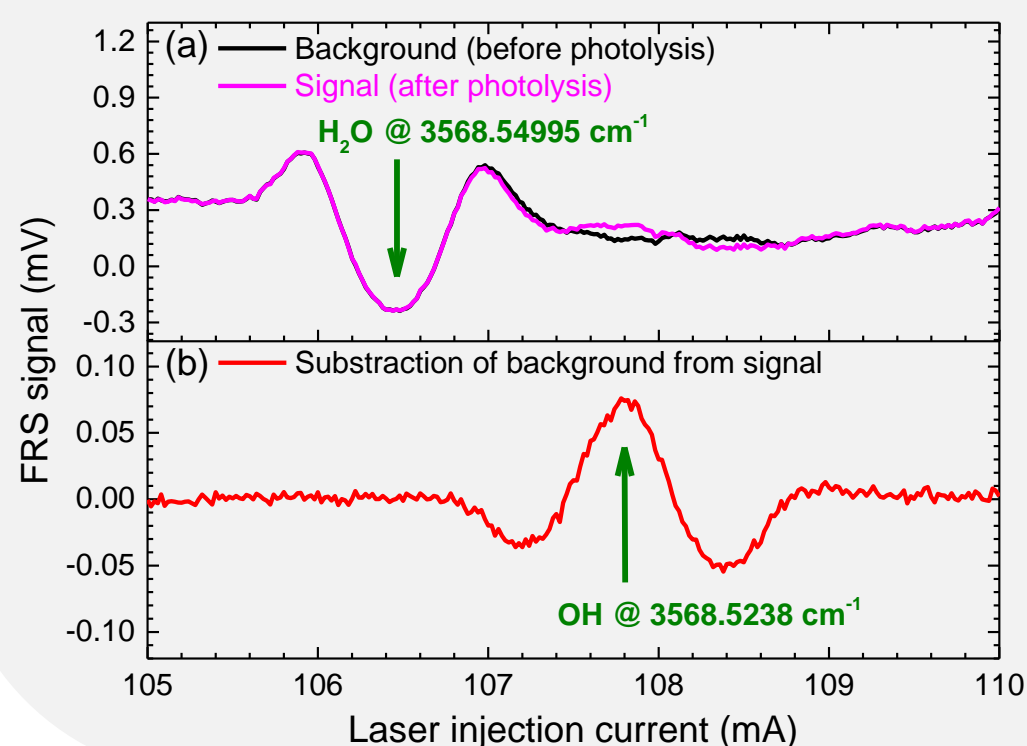
The instrument consists of two parts: an FRS spectrometer for real-time in-situ measurement of OH radicals and a LFP device for generating pulses of high concentrations ($\sim 10^9$ molecule/ cm^3) of OH radicals.

Wei, N., et al. (2020). "Time-resolved laser-flash photolysis Faraday rotation spectrometer: a new tool for total OH reactivity measurement and free radical kinetics research." *Analytical Chemistry* 92(6): 4334-4339.

Data acquisition



Timing scheme of data acquisition and laser photolysis for one laser photolysis pulse. (a) TTL signal generated by function generator for DAQ card data acquisition. Data record begins to record from the rising edge of the TTL and ends at the end of the falling edge. (b) Delayed pulse generated by a digital delay generator for triggering photolysis pulse. (c) Experimental time-resolved FRS signal for OH decay (average signal of 40 pulses), exponential fit, and the corresponding fit residual.



A special background subtraction technique was used.

(a) FRS 2f signals (40 pulses average) before (black line, no OH absorption, used as background signal) and after (magenta line, with OH absorption) laser photolysis. (b) OH signal. After subtracting the background from the signal, the absorption of OH was clearly observed ($[\text{OH}] \sim 4 \times 10^8$ molecule/ cm^3). The point-by-point method was used for the laser wavelength tuning.

This method strongly suppressed laser noise, optical interference, and the absorption of the precursor, allowing the instrument to achieve a very high performance.

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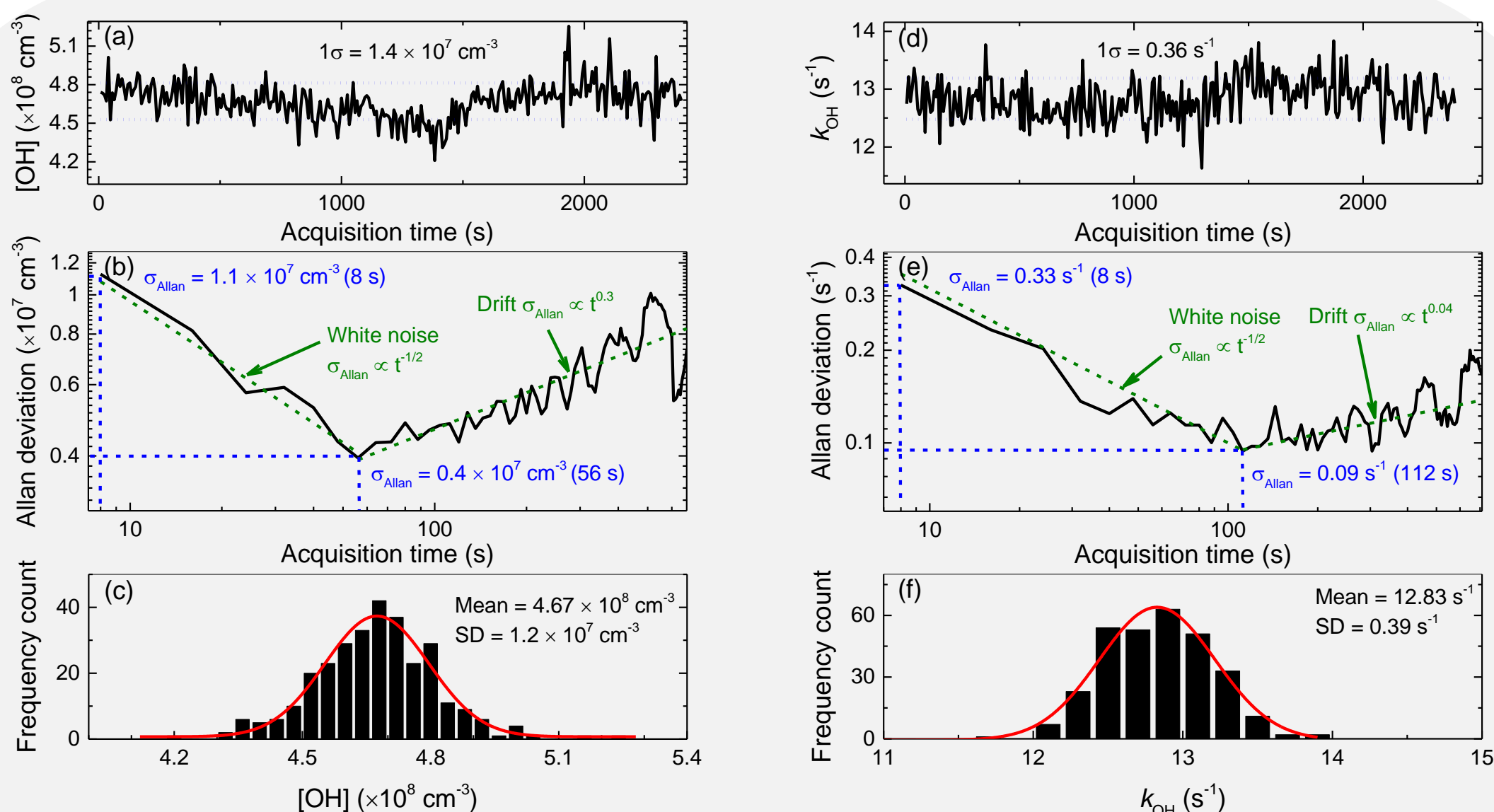
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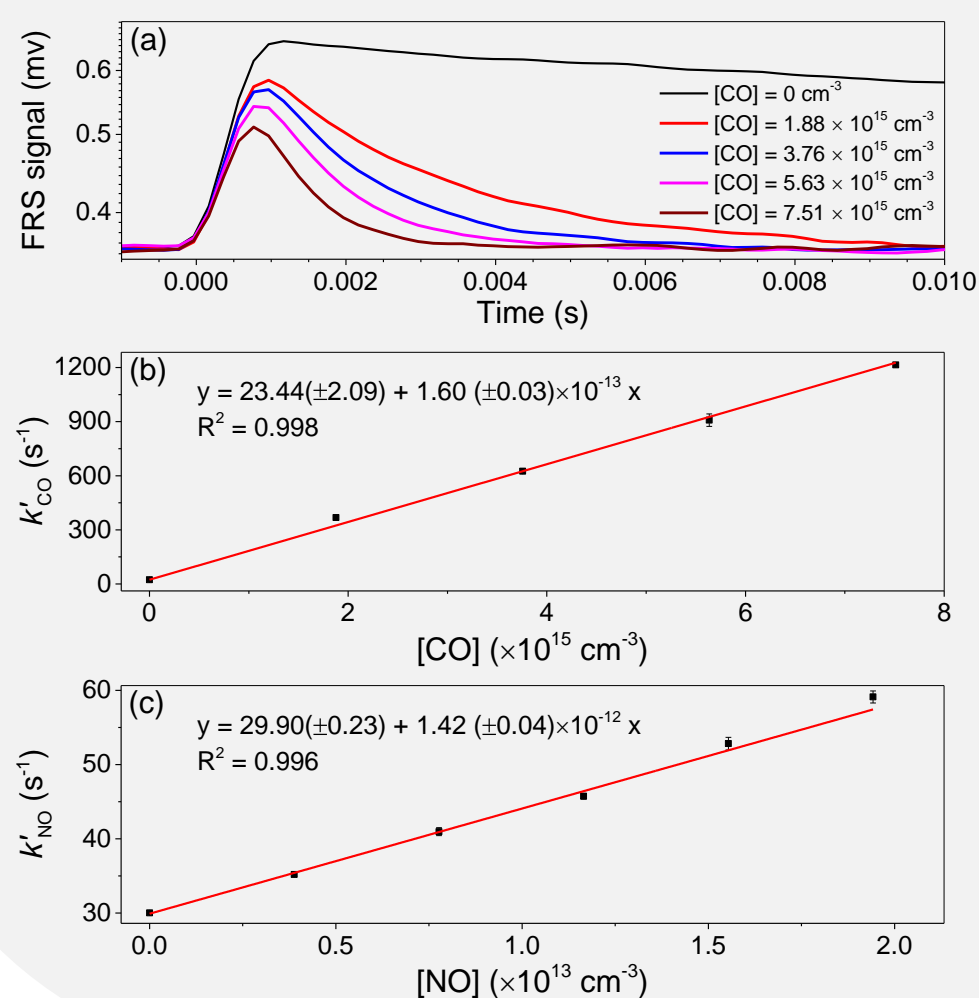
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Performance evaluation of the LFP-FRS instrument



Performance evaluation of the LFP-FRS instrument for [OH] (a-c) and k_{OH}' (d-f) measurements with zero air. The optimum precisions (1σ) of OH concentration and k_{OH}' measurement were $4 \times 10^6 \text{ molecules cm}^{-3}$ and 0.09 s^{-1} over data acquisition times of 56 and 112 s, respectively.



The performance of the system was evaluated by the reaction of OH with CO and NO. The measured rate coefficients ($k_{\text{OH}+\text{CO}}$ and $k_{\text{OH}+\text{NO}}$) were in good agreement with values reported in the literature.

The LFP-FRS instrument provides a new, high precision, and highly selective tool for radical chemistry research. It is not only applicable to the OH radical and can be extended to other transient paramagnetic free radicals such as the HO_2 radical.

With the rapid development of laser, detector, and electronics, this laser spectroscopy instrument can be made more compact and affordable. This work provides a reliable method with low maintenance costs for field k_{OH}' applications. Further improvements will make long-term and network observations possible.