

# High resolution infrared spectroscopy as diagnostic tool for combustion and plasma chemistry

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## INTRODUCTION

Monitoring of transient species within combustion experiments (laminar flames, shock-tubes, flow reactors, etc.) is still relatively challenging task especially if application of non-invasive, i.e. optical detection methods is required. High resolution infrared spectroscopy is based on observation of the fine rotation structure that accompanies vibration transitions and thus provides direct information essential to characterization of both molecular structure and reaction dynamics. Thanks to its outstanding advantage enabling unambiguous assignment of specific molecular system according to its spectral feature, it can serve as a helpful tool for exploring complex reaction mechanisms as well as chemical reactivity of individual species present in laboratory flames or plasmas.

Previous studies gaining new insights into combustion and plasma chemistry as well as our recent advances targeted towards application of high resolution infrared spectroscopy for species concentration measurement in laminar flames are summarized here below.

## FOURIER-TRANSFORM INFRARED SPECTROSCOPY IN POSITIVE-COLUMN DISCHARGE

Hydrogen cyanide (HCN) and its unstable linear isomer HNC are being the subjects of specific interest in combustion chemistry. It was concluded very recently, that introduction of the isomerization reaction (followed by the rapid oxidation of HNC by NO<sub>2</sub>, O, and OH) into conventional NO formation mechanism can quantitatively simulate measured kinetic data [1, 2]. More detailed knowledge about reactivity of suitable HNC precursors for chemical kinetic experiments relevant to combustion chemistry is therefore highly desirable. Decomposition of acetonitrile (He/H<sub>2</sub>/CH<sub>3</sub>CN mixture) in positive column discharge was investigated by the means of time-resolved FTIR emission spectroscopy [3].

Formation of the CN radical, HCN hydrogen cyanide and its isomer HNC were identified in measured emission spectra and their temporal evolution (in microsecond scale) were determined (Fig. 1a)). Same methodology as in the case of acetonitrile discharge was employed to study reaction mechanism and transient species relevant to decomposition of fluorinated fire extinguishing agents [4]. In the given context heptafluoropropane (CF<sub>3</sub>CHF<sub>2</sub>CF<sub>3</sub>) diluted in helium was used as an initial mixture and rovibrational spectra of CF (*X<sup>2</sup>II*) and CF<sub>2</sub> radicals were successfully assigned, see Fig. 1b). Predicted positions of the rovibrational transitions were performed employing the Pickett's SPFIT/SPCAT and DPFIT/DPCAT software suite. Spectral line positions were determined based on fitting procedure according to molecular constants (i.e. spectroscopic parameters) for the ground and excited states taken from the literature [5-7].

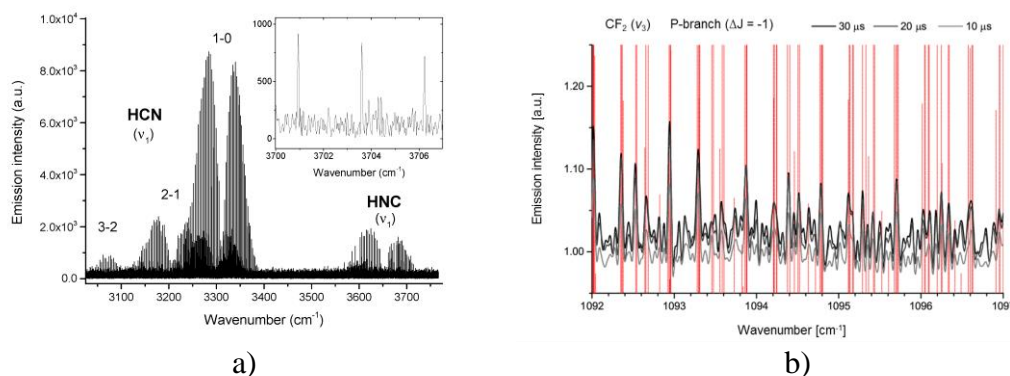


Fig. 1 a) Emission spectrum of positive column discharge of H<sub>2</sub>/CH<sub>3</sub>CN/He, b) temporal evolution of high-resolution spectra of CF<sub>2</sub> radical as obtained from time-resolved FTIR measurement. Predicted spectral line positions belonging to P-branch transitions of the asymmetric stretching (v<sub>3</sub> mode) vibration are depicted as vertical red lines

For both experimental cases (He/H<sub>2</sub>/CH<sub>3</sub>CN as well as He/CF<sub>3</sub>CHF<sub>2</sub>) reaction mechanisms appropriate to discharge processes were proposed and results of chemical kinetic modelling were compared to measured data according to procedure described in [8].

## TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY IN HOLLOW CATHODE DISCHARGE PLASMA

Several fundamental transitions of carbon monoxide from its excited vibrational states in the 1970 cm<sup>-1</sup> region were detected in hollow cathode discharge of He/CO mixtures employing experimental arrangement depicted in Fig. 2.

So called concentration modulation (or “on-off” modulation) technique was used to identify spectra of excited CO molecule suitable for monitoring in combustion-related conditions. The advantage of this procedure consists in the utilization of a modulated a.c. (order of tens to thousands Hz) discharge; a signal from the detector being processed by means of the phase-sensitive (lock-in) amplifier that evaluates its 1f harmonic component.

Intensities of rovibrational lines derived from IR TDLAS experiment enable to determine energy distributions in hollow cathode discharge and laminar flame environment respectively. Such information is crucial in order to setup parameters of plasma adequately according to plausible conditions relevant to low-temperature oxidation process.

Experimental investigations on important combustion intermediates (e.g. when searching for ketene and its role in formation of carbon suboxide in diethyl ether cool flames) are further planned to be performed in this direction.

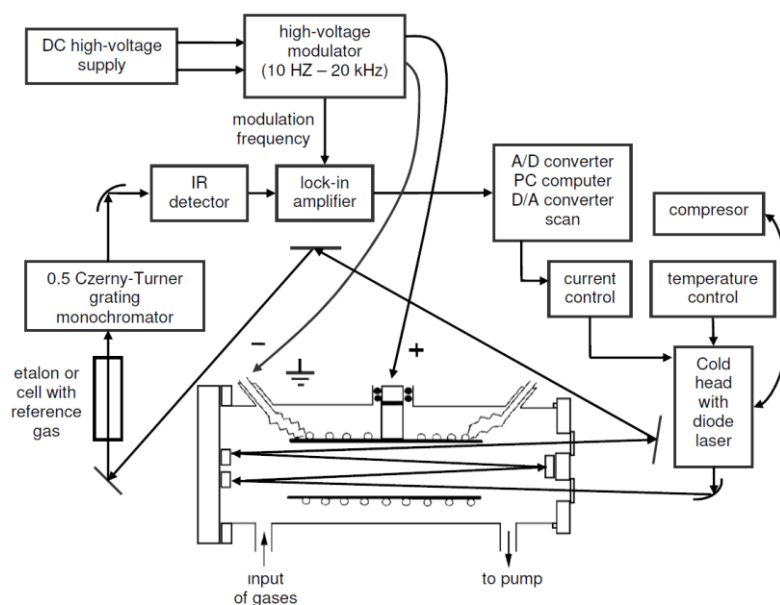


Fig. 2 Experimental set-up for IR laser diode spectroscopy of transient species produced in hollow cathode.

## TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY IN ATMOSPHERIC PRESSURE LAMINAR FLAMES

Laminar flames are often utilized e.g. for benchmarking the performance of chemical kinetic models [9] as well as for laboratory-scale testing of the techniques suitable for practical diagnostics in industrial combustion devices.

Following our previous studies on plasma properties (electron temperature measurement [10]) of laminar premixed flames we further explored feasibility of TDLAS ( $2f$ -WMS technique) for monitoring species concentrations in high-temperature oxidation at atmospheric pressure. First overtone transitions of the OH radical in the near-infrared region, namely between  $6355\text{ cm}^{-1}$  and  $6365\text{ cm}^{-1}$ , were reinvestigated in the given context following the findings from previous studies [11, 12]. Predictions of spectral features were obtained by the aid of HITEMP database [13] for the given purpose. Results of numerical simulations in one-dimensional representation employing CANTERA software toolkit were used to estimate a flame structure (i.e. temperature and species concentration profiles). Measurements were performed in atmospheric pressure laminar premixed flame burning dimethyl ether-air mixture at fuel-lean conditions (equivalence ratio  $\Phi = 0.73$ ).

Complex spectral features of high-temperature water vapor absorption lines in the given region (around  $1.57\text{ }\mu\text{m}$ ) is one of the main factors limiting straightforward determination of spatially resolved absolute concentrations of OH radicals in flames. Two doublets of well resolved spectral lines with significant difference between the scans through reaction zone and post-flame region were unambiguously assigned to rovibrational overtone ( $\nu = 0 \rightarrow \nu = 2$ ) transitions belonging to hydroxyl radical in its ground ( $X^2II$ ) state.

Moreover, it was revealed that rovibrational lines with absorbance on order of  $10^{-4}$  are easily accessible in our experimental setup using short optical path-length (of few centimeters). These findings open up the way to practical applications of  $2f$ -WMS technique for laboratory scale non-invasive combustion diagnostics in laminar premixed and nonpremixed flames using standard configurations of flat-flame or counterflow burner.

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