

**DIAGNOSTICS AND MODELING OF GLOW DISCHARGES
BY TIME RESOLVED IR ABSORPTION SPECTROSCOPY**

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Abstract

In this work several applications of time resolved absorption spectroscopy, with different time scales and spectral resolutions, are described for the diagnostic and modeling of cold plasmas produced in square wave modulated hollow cathode discharges. These methods have revealed very sensitive and efficient to test the relevance of the different individual mechanisms, in comparison with the usual plasma diagnostic methods of the stationary state.

1. Introduction

Over the last two decades, the use of plasmas produced by glow discharges has experienced a growing interest in many scientific and technological fields. Dissociation processes in these plasmas, performed primarily by electronic collisions with the gas species and followed by a great variety of secondary mechanisms, can lead to chemical conditions partially equivalent to those obtained at high temperature and are now currently employed in thin film processing by plasma assisted chemical vapor deposition (PACVD), surface conditioning of different materials and vacuum vessels [1-3], light sources, and even in new techniques for pollution control [4]. These “cold”, partially ionized plasmas, are non-equilibrium systems characterized by a comparatively hot electron energy distribution (with mean energies of several eV), very energetic ions (hundreds of eV), suitable to produce sputtering when impinging on the electrode surfaces, and much colder (close to room temperature) energy distributions for the neutrals. From the scientific point of view, the exact diagnostics and characterization of these plasmas is still a challenge, in addition they are very useful for the production of unstable species such as radicals, ions and excited states of neutral atoms and molecules, allowing for a better knowledge of the properties and behavior of these species, of interest in fields like the modeling of the chemical self-cleaning

capability of the troposphere, mainly due to very reactive radicals such as OH or NO₃ [5], or in the identification of several interstellar species [6].

Nevertheless, the complex kinetics of these plasmas is extremely difficult to disentangle, since it includes electron impact dissociation, ionization and excitation, non reactive quenching, gas phase homogeneous chemistry, heterogeneous wall reactions, diffusion, etc.; and, due to the scarcity of data for many of the relevant elementary processes, a theoretical modeling of these systems and a prediction of their performances are usually far from satisfactory. As a rule, a thorough experimental diagnostics is needed in order to make sound advances in the modeling.

Concerning the experimental methods used commonly to study glow discharges, electrostatic probes represent the most universal and simple cold plasma diagnostic, whereas mass spectrometry is a standard technique used in most of the plasma laboratories, specially in its differentially pumped version. But major interest should be devoted to the optical spectroscopic methods, which are particularly suited to test the plasma behavior, since they are non intrusive, allow high sensitivity and selectivity, enable position resolved experiments and provide a remarkable higher temporal resolution than the other experimental techniques. Emission and actinometry have been the most commonly used spectroscopic methods for plasma diagnostics, employed usually in the UV or the visible regions of the electromagnetic spectrum. Their basic limitations arise from the fact that only those species which are excited by the plasma particles are detectable and absolute calibration of the concentration of the involved species is usually a very difficult task. These problems are overcome by the use of absorption spectroscopy, where ground state molecules are detected, with light sources and detectors of the required wavelength. Besides, absolute concentrations are directly inferred. But although this technique has a high potential for cold plasma characterization, only few measurements have been reported thus far.

In the present article, the activity of the plasma group of the Instituto de Estructura de la Materia at the CSIC in the field of plasma diagnostic by absorption spectroscopy in the IR region is reviewed. This work has been devoted mainly to research on plasmas of nitrogen oxides and methane, complemented with IR emission measurements, double Langmuir probes and quadrupole mass spectrometry. The measurements include several stable molecules and radicals. Major emphasis is made in the study of plasmas produced in square wave modulated, hollow cathode discharges, at comparatively low frequencies of modulation, and their characterization by time-resolved procedures. As it will be shown, modulation of the discharge at different frequencies and time resolved diagnostics at different

time scales provides a very valuable information about the temporal hierarchy of the characteristic dynamical features involved in the global kinetics of the plasma.

Experimental Methods

The mid infrared spectral region is very suitable to investigate cold plasmas, since the vib-rotational transitions of a great deal of molecular species are mostly found in this region. Nevertheless, due to the intrinsic complexity of the spectrum of each individual species and to the abundance of different species usually found in glow discharges, high resolution spectrometers are frequently needed to characterize them unquestionably. The spectral resolution limit is imposed by the natural line-width of the individual transitions, which at the usual operating pressures (≤ 1 mbar) depends only of the Doppler broadening, proportional to the spectral frequency, in such a way that the IR region supplies the additional advantage of a narrower line-width as compared with the visible or the UV region. Besides, in contrast with other plasmas, neutral particles in glow discharges are close to ambient temperature, and line-widths about 10^{-2} cm^{-1} are not usually exceeded, even for the lighter molecules. On the other hand, if the unstable species produced in the discharge were to be detected, very sensitive and selective techniques would be needed, since their concentrations are usually several orders of magnitude smaller than those of the stable products.

In order to achieve useful time resolved information on plasma processes, an appropriate choice of the frequencies of modulation of the discharge and of the temporal resolution of the diagnostic techniques are of the major importance; but, besides the dependence on cross sections related with each individual mechanism, the speed of the processes depend on the physical characteristics of each particular discharge: pressure, gas flow rate, geometry, electrical power, temperature, materials of the wall and the electrodes, etc.; therefore, a previous estimation of the time scales is usually far from trivial.

The probability of interaction P_{ab} between two species a and b in the gas phase is proportional to the product $P_{ab} = n_a \times n_b \times \sigma_{ab} \times v_{ab}$ ($\text{cm}^{-3}\text{s}^{-1}$), where n_a and n_b are the respective concentrations of a and b , σ_{ab} is the cross section for the interaction and v_{ab} is the relative velocity of the colliding species. Usually the value $k_{ab} = \sigma_{ab} \times v_{ab}$ is named the rate-constant, dependent of temperature.

Electron densities can be assumed to appear instantaneously at the ignition of the discharge, in comparison with the time scales of the processes to be considered. Regarding dissociation by electronic impact, responsible for the ignition of the discharge, electrons, with temperatures $T_e \sim 10^4$ K and mean energies $\sim 1-10$ eV [1] remain near threshold for the dissociation processes of a large number of light species [7], and rate dissociation constants

$\sim 10^{-9}$ – 10^{-11} cm³ molecule⁻¹ s⁻¹ are usually found, corresponding to quite small cross sections for the large mean electron velocities implied, ~ 1000 km/s. With these values and typical electron densities about 10^{10} cm⁻³, characteristic times of the dissociation processes are of the order of seconds. On the contrary, cross sections for bimolecular reactions can reach the molecular dimensions ($\sim 10^{-15}$ cm²) in those cases where very reactive species such as radicals or excited atoms are involved. Nevertheless, due to the low temperature of the neutrals in the plasma (~ 300 K) and to their thermal velocity distributions, the rate constants turn out to be comparable to those of dissociation by electronic impact. Therefore, in view of the low concentrations of very reactive species ($\sim 10^{10}$ – 10^{12} cm⁻³), characteristic times are not smaller than seconds. On the other hand, electron impact excitation can be two or three orders of magnitude more efficient than dissociation, especially when resonances are involved; therefore characteristic time constants for electron impact excitation can be considerably shorter than those of the former processes and reach the milliseconds or even smaller values.

The contribution of diffusion becomes also important because, frequently, several spatial regions are distinguished in glow discharges. Characteristic diffusion times “ τ ” depend of the diffusion coefficients “D” and the size of the plasma regions (where “L”, the fundamental dimension, is of the order of the smallest diffusion length),

$$\tau = \frac{L}{\sqrt{2D}} \quad D(\text{cm}^2\text{s}^{-1}) = 0.00263 \frac{\sqrt{T^3 / M}}{Pd^2}$$

At the usual conditions in these plasmas, with $T \sim 300$ K, the diffusion coefficient D for light species $M \sim (10-50)$ a.m.u, with typical molecular diameters, $d \sim 3-5$ Å, varies between $0.1/P$ and $1/P$. Therefore, for a typical maximum pressure in glow discharges, $P \sim 10^{-3}$ bar, characteristic times for molecules diffusing $L \sim 5$ cm are $\tau \sim 0.1-0.3$ s, and these τ values can decrease one or two orders of magnitude for smaller P and L values. Finally, the residence time inside the cell should be considered too, its value depending on gas flow rate and reactor volume.

In agreement with the formerly estimated characteristic times, experimental time resolutions between 10^{-3} and 1 s and modulation frequencies of the glow discharges between some tenths and some tens of Hz are very appropriate to investigate the kinetics of the plasma; these frequencies can be applied to turn on and off DC discharges, but can be also used to modulate the amplitude of RF or MW discharges, in order to extend to them the time resolved studies.

In this article some of the work with two hollow cathode, low frequency modulated, reactors, both refrigerated by water, devoted to study quite different magnitudes involved in the kinetics of CH₄ and N₂O plasmas by time resolved absorption spectroscopy, is described, in order to demonstrate the possibilities of the method. The CH₄ and N₂O reactors have very different sizes and geometries and have been studied with an infrared, high resolution (10⁻³ cm⁻¹) laser spectrometer and a medium resolution (0.1 cm⁻¹) FTIR spectrometer, respectively. In CH₄ discharges, characterization of the temporal behavior of the chemically unstable CH₃ radical allows the determination of its absolute concentration in the sample and provides an experimental method to estimate sticking coefficients on the surfaces of the cathode wall. The study of N₂O discharges at different time scales exemplifies the capabilities to diagnose the relevance of some elementary mechanisms, in a much more sensitive way than diagnostics of continuous discharges. The two experimental set-ups are shown in Fig. 1.

Fig. 1.a shows the difference-frequency laser spectrometer built in our laboratory, with a wavelength coverage of 2.2 to 4.5 μm, and 1 μW IR power, as well as the 1 m long hollow cathode reactor with an optical multipass White cell configuration. Its detailed description is found elsewhere [8,9]. The spectroscopic system is arranged to get high detection sensitivity by means of high frequency modulation (15 kHz) of the laser beam, phase sensitive detection of the sample absorption and the reference signals, and continuous normalization by division of both signals. The selected time constant of the lock-in amplifiers (1 ms) determines the temporal resolution on the spectroscopic system. Stabilization of the spectrometer at a fixed resonant wavelength and additional on/off modulation of the hollow cathode discharge current at frequencies below 50 Hz allows to study the transients happening inside the plasma. On the other hand, when the spectral wavelength is tuned, a second phase-sensitive detection stage collecting the normalized signal allows to discriminate the continuous absorption spectrum of stable molecules, from the modulated signals of unstable species like CH₃, whose concentrations are several orders of magnitude smaller. In that case, the response of the last lock-in, working at a relative large time-constant (~ 1 s), provides a “variation of transmittance” spectra and, besides the detection of transient species, allows a distinction of the tiny changes in Doppler profiles and in the population of vib-rotational levels of the stable species from discharge on/off; and finally, to estimate the translation and vib-rotational small temperature variations of these compounds.

Fig. 1.b shows the (0.1 cm⁻¹) FTIR Spectrometer used to study the kinetics of a N₂O plasma, produced in a hollow cathode reactor smaller than the former one, specially designed for absorption and emission studies. A detailed description of the experimental system is

found in ref.[10,11]. The length of the reactor cell (22 cm) fits the sample compartment dimensions of the spectrometer for a maximum absorption path-length. The FTIR spectrometer (Bruker IFS66) allows two modes of operation, related to the sweeping mode of the mirror: the rapid-scan and the step-scan options, whose selection is crucial in the achievement of different time resolution scales. In contrast with other spectral equipments, FTIR spectrometers are unable to operate at a fixed wavelength, but supply always an interferogram from which the whole spectrum is deduced by inverse Fourier Transform, with a spectral range depending on the optical components of the equipment and a spectral resolution depending on the total distance traveled by the moving mirror. Therefore, time-resolved measurements in these cases imply always obtaining three dimension (intensity, wavelength and time) spectra, from which the temporal evolution of a given species at a given wavelength can be obtained. Data collecting techniques differ markedly between the rapid-scan and the step-scan options of FTIR spectrometers. In the rapid-scan option, each interferogram is finished before a new one is started and meanwhile the signal should not change appreciably; therefore, temporal resolution depends on the spectral resolution (i.e. displacement of the moving mirror at a constant velocity), and is usually quite low (tens of ms – s) . In the step-scan option, the mirror stands at a fixed position during the data collection of each whole transient signal, sampling it at constant time intervals, and then moves to the next position until its entire displacement is completed. After that, each interferogram is built from the data sets at the different mirror positions, at each time of interest of the transient. This is the named “interleaving technique”, where maximum temporal resolution depends only of the detector and hardware time responses, and values in the range of μs are attainable.

3. Experimental results

In Fig. 2, a small part of the high resolution spectra of a pure CH_4 discharge (2 mbar, 7 mbar.l/s, 90 mA, 800 V, 18 Hz), obtained with the difference frequency IR laser spectrometer and the experimental set-up shown in Fig. 1.a can be seen. Fig. 2.a shows the transmittance spectrum of the discharge, obtained from the first phase-sensitive detection stage of the acquisition system; in it, only two lines of the precursor CH_4 and a weak line of one of the stable products, C_2H_4 , can be seen. Spectra taken at neighboring wavelengths (not shown in the figure) allows the detection of C_2H_6 in the methane discharge too. Fig. 2.b shows the much weaker modulated variation of transmittance spectrum obtained with the second phase-sensitive detection stage, showing the 5153.324 cm^{-1} , ${}^1\text{Q}_0(4)$ line of the ν_3 band of CH_3 , as well as the CH_4 lines displayed in the upper panel and two other lines belonging to

CH₄ hot band transitions. The CH₃ signal indicates the appearance of the radical in the discharge “on” half-periods and its disappearance during those of discharge “off”. The signals in Fig. 2.b corresponding to stable compounds reveal small changes in width and population of their rotational levels due to temperature changes as low as ~ 15 K between discharge on and off. Due to its very large sensitivity, this method has allowed us not only to characterize the methane discharge, but also to detect and identify hot lines of the precursor not observed before [9].

Fig. 3 shows the decay of the concentration of CH₃ deduced from its ¹Q₀(4) absorption, averaged during 256 turn off half-periods of the modulated CH₄ discharge. In CH₄ plasmas, the CH₃ radical is known to disappear only by homogeneous recombination (k_1) into ethane and by sticking at the reactor surfaces, influenced by diffusion and surface loss (k_2), following the time dependent expression given in Fig. 3. Knowing $k_1 = 4.5 \cdot 10^{-11} \text{ cm}^3/\text{molec.s}$ [12], a best fit of this expression to the experimental results of Fig. 3 provided a CH₃ concentration $n_0 = (1.7 \pm 0.03) \cdot 10^{12} \text{ cm}^{-3}$; i.e. ~0.01% that of the precursor [13]. On the other hand, this fit led to a value $k_2=144 \text{ s}^{-1}$; with this value, taking into account diffusion, mainly in CH₄, and the Chantry formulation [14], a sticking coefficient for the stainless steel of the hollow cathode at ambient temperature $S=(3.3\pm 0.6)\times 10^{-2}$ was inferred [15]. Although the conditions of the cathode wall in this experiment were not exhaustively characterized, this result shows the possibilities of the experimental method. Sticking coefficients of CH₃ have been scarcely measured before and usually estimates have been used for theoretical simulation of carbonated thin films deposition.

In relation with N₂O plasmas, Fig. 4.a shows a partial absorbance spectrum of a 1 mbar, 0.05 mbar l/s, 40 mA, pure N₂O DC discharge with a spectral resolution of 2 cm⁻¹. In this figure, besides some bands of the precursor, the very intense band ν_3 of NO₂ and that of NO produced in the discharge can be appreciated. Fig. 4.b shows a detail at higher resolution of the NO band. The time response of these signals when turning on/off the discharge with an interval of several seconds is seen in Fig. 5, once the absolute concentration data is obtained by band integration of the three dimensional absorbance spectrum taken with the rapid-scan operating mode of the FTIR spectrometer. For the sake of completeness of data, the concentration of the IR inactive homonuclear molecules N₂ and O₂ produced in the discharge, obtained by quadrupole mass spectrometry is also drawn, as well as the prediction of a kinetic model developed by our group to characterize this N₂O discharge [11]. The temporal dependences in this case are mainly due to dissociation and to homogeneous and heterogeneous recombination processes, as well as to the influence of the gas flow rate. On the contrary, Fig. 6 shows the evolution of population of the N₂O ground state in response to

a 45 Hz modulation signal. Fig. 6.a depicts schematically this evolution from the ignition of the discharge, Fig. 6.b represents the experimental results at its “quasi-stationary” state. In this case the fast transients are principally ascribed to excitation and de-excitation N_2O mechanisms and to diffusion processes along the different regions of the discharge [16].

4. Conclusions

In this work, the advantages of time-resolved absorption spectroscopic techniques for plasma diagnostics are described; with them, several fundamental characteristics of the discharges can be estimated in a much more precise way than with the simple study of their stationary states, as it is shown by the various examples taken on the different plasmas and the different techniques.

Acknowledgments

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References

- [1] Grill A. *Cold Plasma in Materials Fabrication*, IEEE Press: New York, 1993.
- [2] Gordillo FJ, Albella JM. *Rev. Esp. de Física* 1998;12:25.
- [3] Tabarés FL, Tafalla D, de la Cal E. *Recent Res. Devel. Vac. Sci. & Tech.* 1999; 1:93.
- [4] Penetrante BM, Schultheis SE. *Non-thermal Plasma Techniques for Pollution Control*, NATO-ASI Series G: Ecological Sciences 34, 1992.
- [5] Wayne RP. "Chemistry of atmospheres", Clarendon Press, Oxford 1991.
- [6] Cernicharo J, Liu X, González-Alfonso E, Cox P, Barlow MJ, Lim T, Swinyard B. *Astrophysical Journal Letters* 1997, 487: L65
- [7] Radzig AA, Smirnov BM. *Reference Data of Atoms, Molecules, and Ions*, Springer-Verlag, Berlin 1985.
- [8] Bermejo D, Domenech JL, Cancio P, Santos J, Escribano R; *Laser Spectroscopy IX*, Academic Press, New York 1989.
- [9] Tanarro I, Sanz MM, Bermejo D, Domingo C, Santos J. *J. Chem. Phys.* 1994; 1: 238.
- [10] Arcos T, Domingo C, Herrero VJ, Sanz MM, Schulz A, Tanarro I, *J. Phys. Chem. A* 1998; 102: 6282.
- [11] Arcos T, Domingo C, Herrero VJ, Sanz MM, Schulz A, Tanarro I. *J. Phys. Chem. A* 2000; 104: 3974.
- [12] Toyoda H, Kojima H, Sugai H; *Appl Phys. Lett.* 1989;54, 1507.
- [13] Tanarro I, Sanz MM, Bermejo D, Domingo C, Santos J, Domenech JL. *J. Phys. Chem.* 1994; 98: 5862.
- [14] Chantry PJ; *J. Appl. Phys.* 1987; 62:1141.
- [15] Sanz MM; Thesis, U. Complutense de Madrid, 1995.
- [16] Arcos T, Castillo M, Domingo C, Herrero VJ, Sanz M M, Tanarro I; *J. Phys. Chem. A* (submitted).

Figure captions

Fig. 1 – Schemes of the two experimental systems described in this work for time resolved IR absorption spectroscopy. a) The difference frequency IR laser spectrometer and the 1 m long, hollow cathode reactor provided with an optical multipass White cell configuration, for the study of CH₄ plasmas and the methyl radical. b) The FTIR spectrometer containing in its absorption sample holder the hollow cathode discharge cell, 22 cm long, in a single optical path configuration, used for the diagnostic of N₂O plasmas. BS: beam splitter, MM: moving mirror, FM: fixed mirror. The emission option is also shown.

Fig. 2 – Spectra of the CH₄ discharge, obtained around the 5153.324 cm⁻¹ line of the CH₃ radical with the difference frequency IR laser spectrometer and the experimental set-up shown in Fig. 1a. a) The transmittance spectrum: only two lines of the precursor CH₄ and a weak line of one of the stable products, C₂H₄, can be seen. b) The modulated variation of transmittance spectrum, showing the ¹Q₀(4) line of the ν₃ band of CH₃, as well as the same CH₄ lines seen in part “a”, together with other lines belonging to CH₄ hot band transitions.

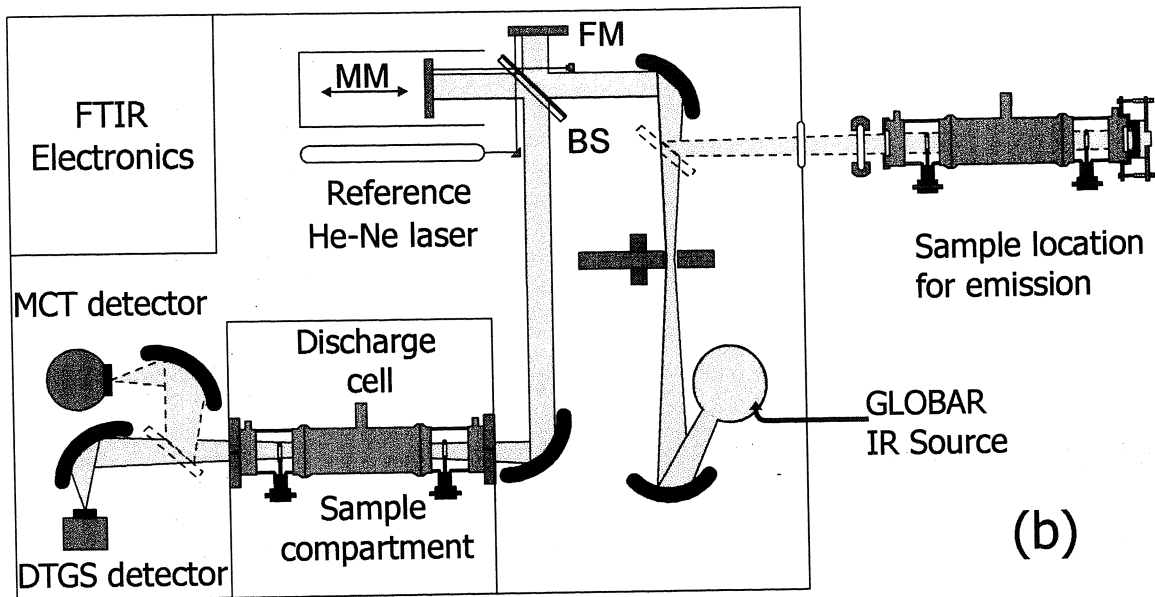
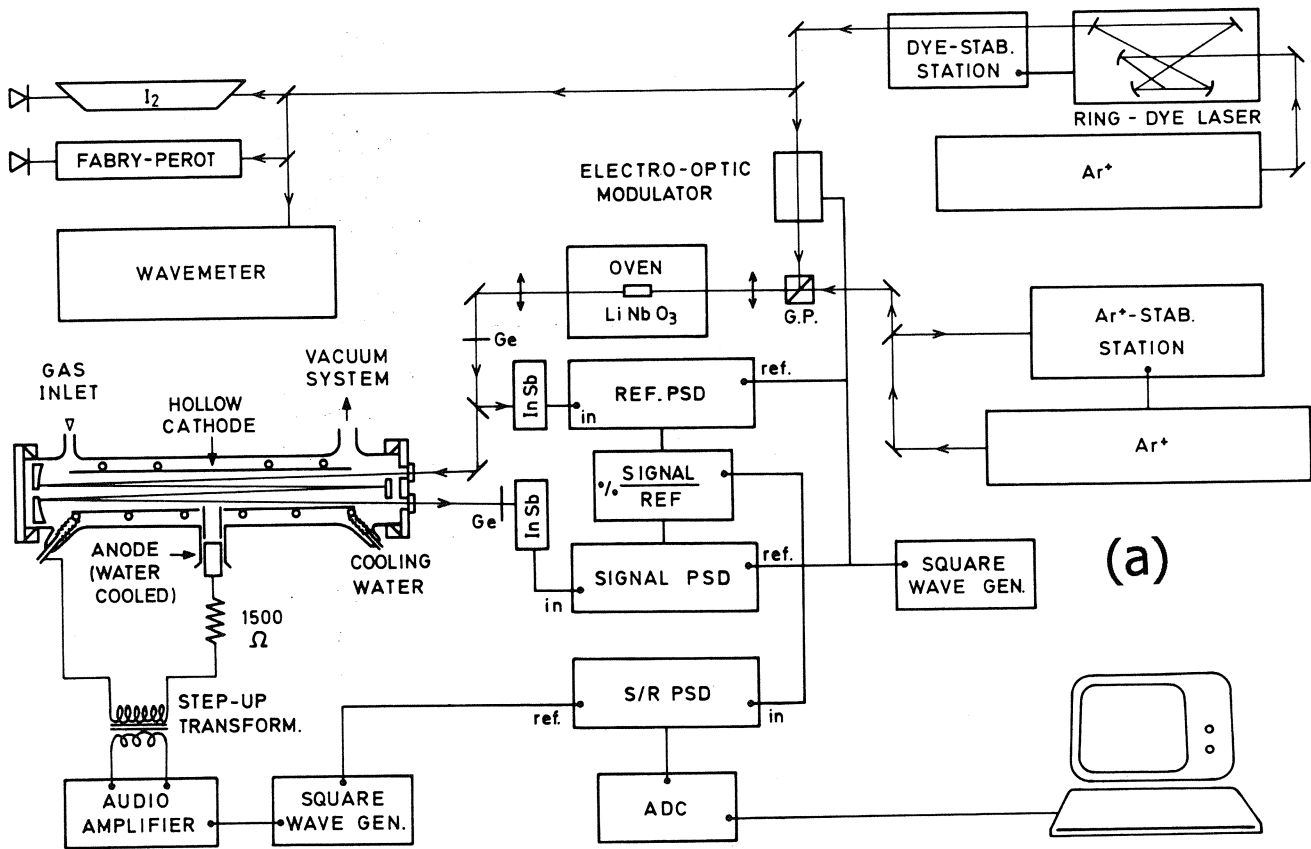
Fig. 3 – Decay of the CH₃ ¹Q₀(4) absorption signal, measured after the sudden extinction of a CH₄ discharge, employed here as a method to estimate the concentration and the sticking coefficient of this radical in the hollow cathode reactor.

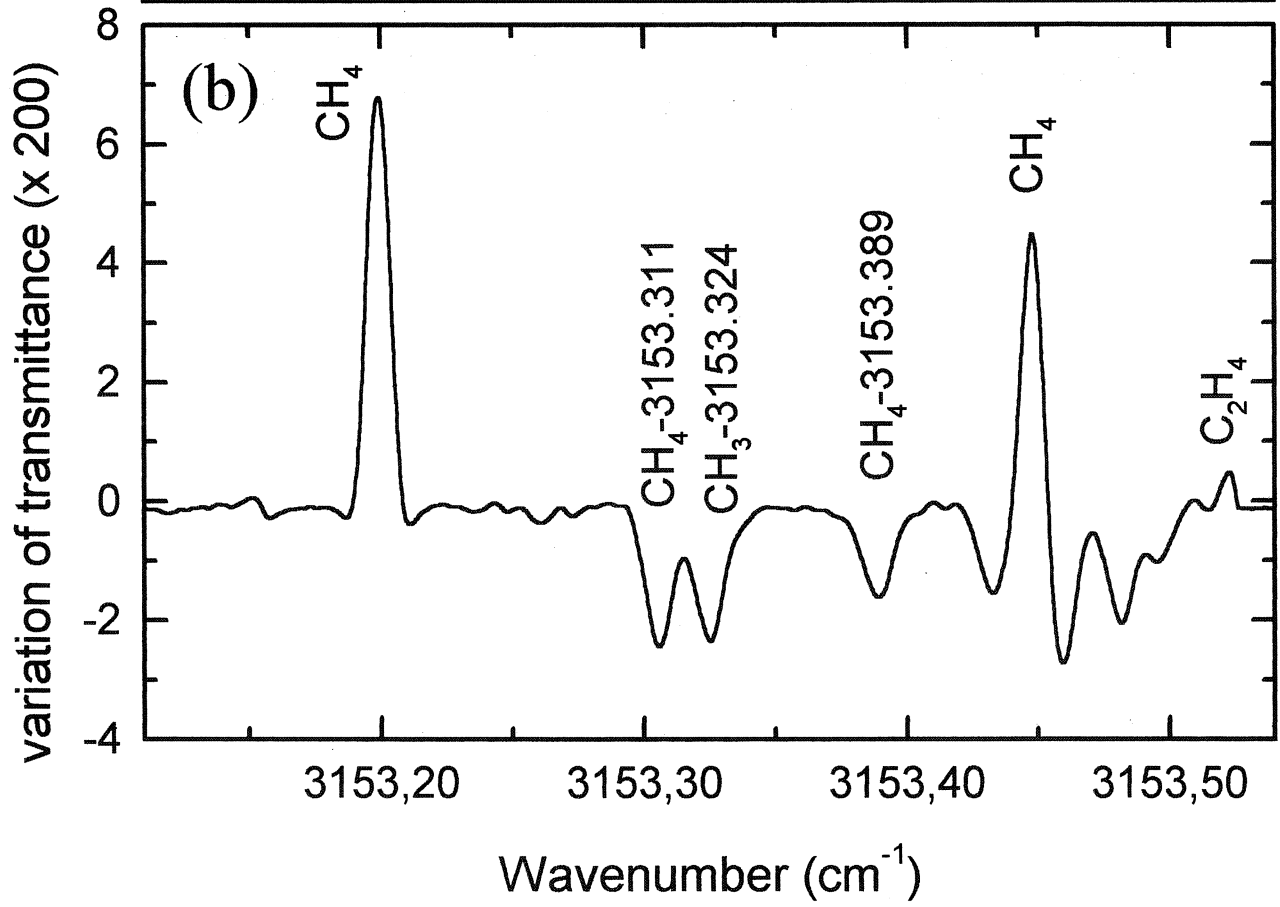
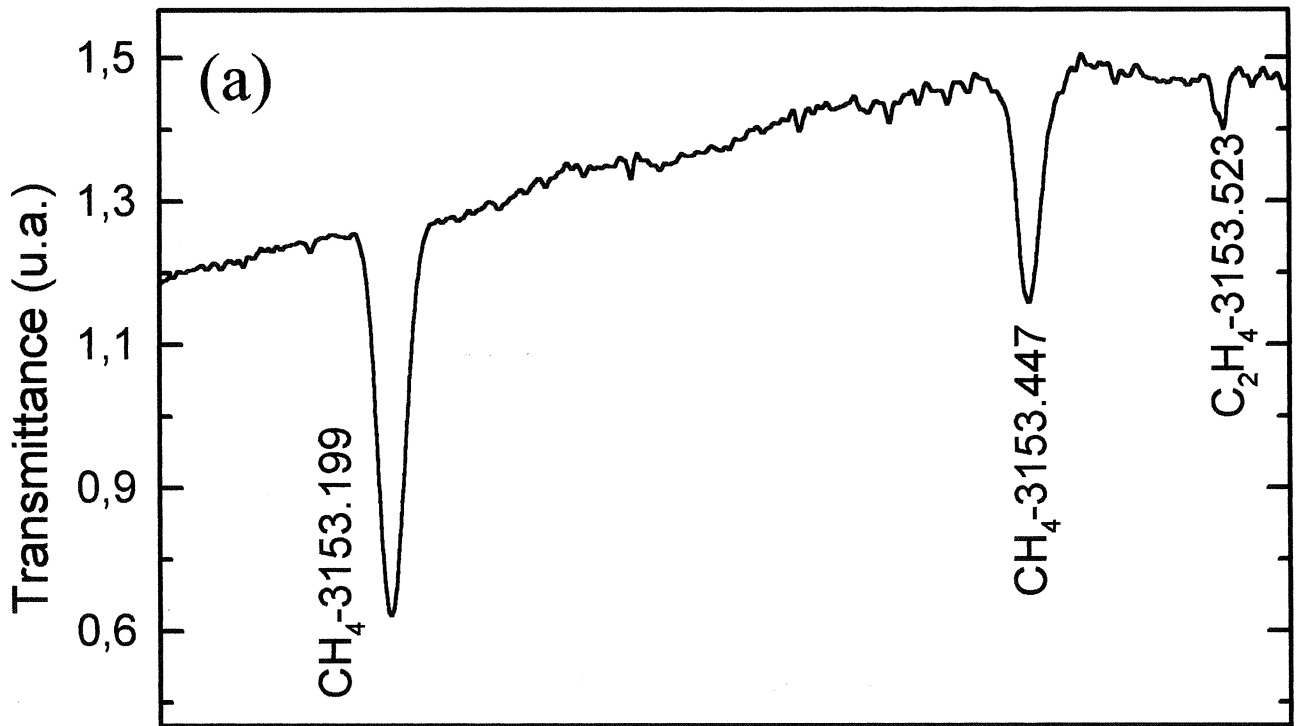
Fig. 4 – Transmittance spectrum of a N₂O, DC discharge, obtained with the FTIR spectrometer and the experimental set-up shown in Fig. 1b. a) The ν₃ and ν₁+ν₂ bands of the precursor, as well as the sole band of the diatomic NO and the very intense ν₃ band of the NO₂ produced in the plasma, with a 2 cm⁻¹ spectral resolution. b) Detail of the NO vib-rotational band at a higher resolution of 0.25 cm⁻¹, the asterisk indicates the N₂O ν₁+ν₂ signal.

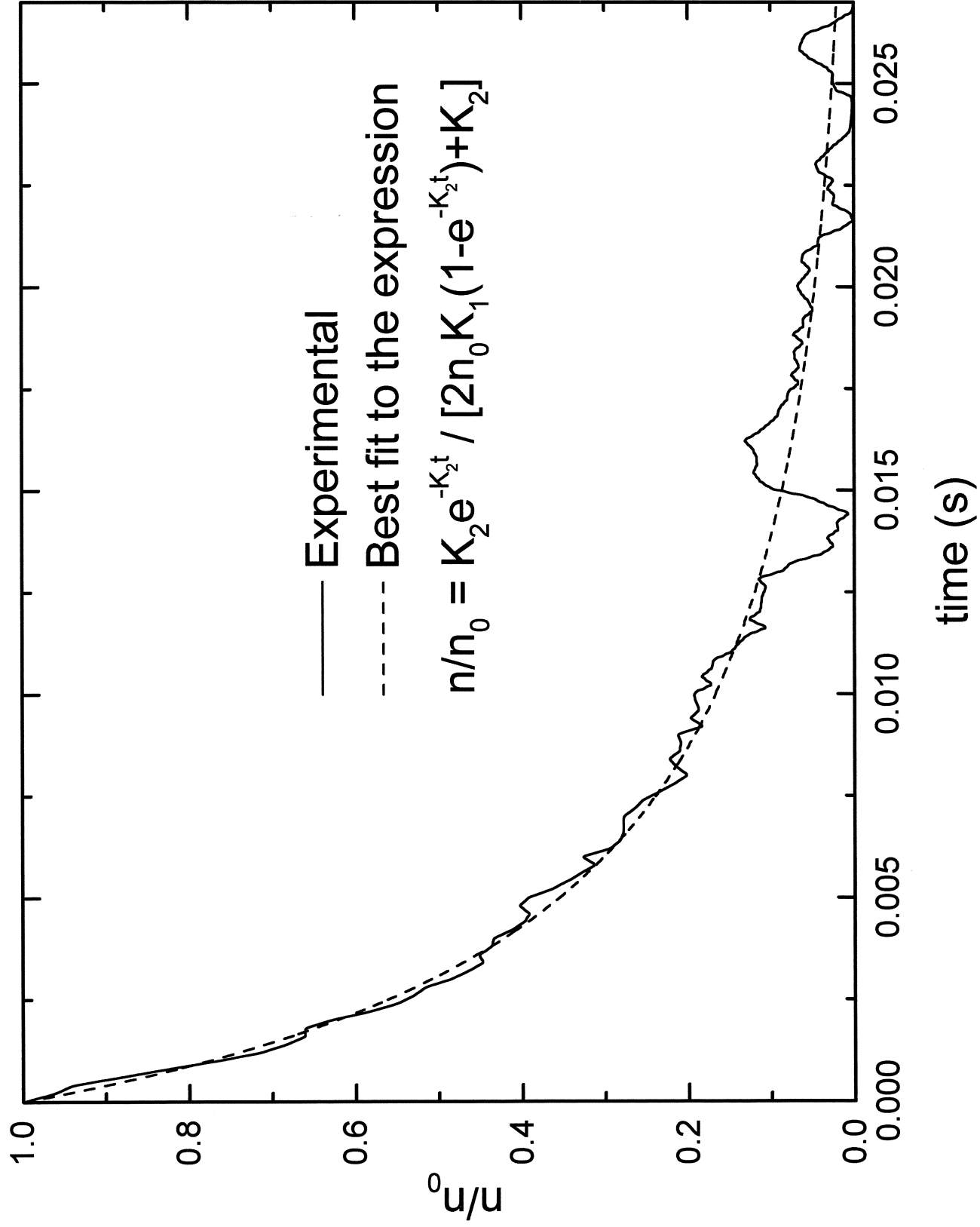
Fig. 5 – Time dependence of N₂O, NO and NO₂ concentrations during turn on/off of the discharge, obtained by integration of their time resolved IR bands, taken with the FTIR spectrometer in the rapid scan mode of operation at time intervals of 100 ms. The concentration of N₂ and O₂, are also shown, as measured by differentially pumped, quadrupole mass spectrometry. The comparison between all these signals and the predictions of the theoretical kinetic model developed by our group can be seen too.

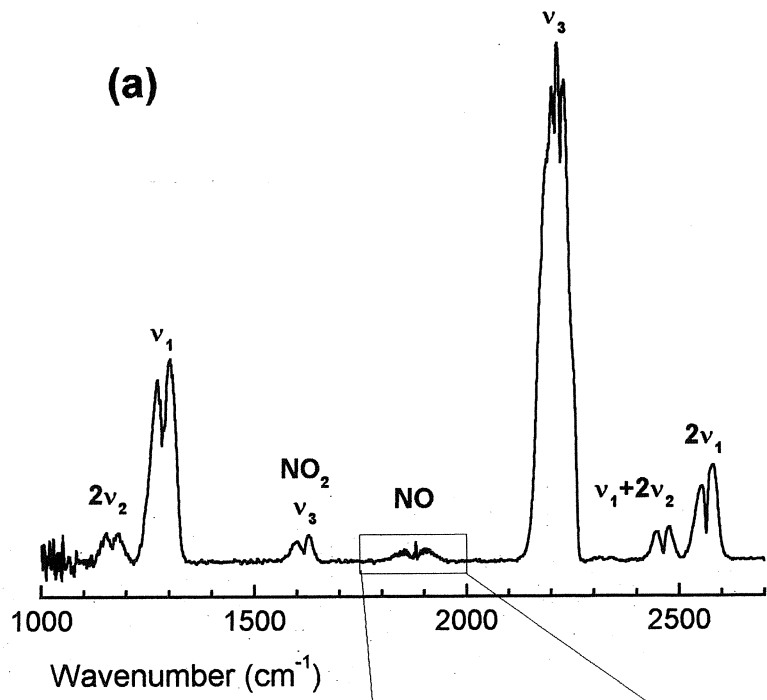
Fig. 6 –a) Qualitative response of the ground state population of the precursor in a modulated discharge, up to the attainment of the “quasi-stationary” state; in it, the quick and small modulation of the signal at the frequency of the discharge, superposed to the larger but slower initial variation in the mean value of the concentration can be

appreciated. b) Temporal evolution of the N₂O ground state population, obtained with the FTIR spectrometer working in the step-scan mode at a time resolution of 0.55 ms, and the hollow cathode discharge cell modulated at 45 Hz, 80 mA (maximum current), 2 mbar, 0.05 mbar l/s of pure N₂O. The measurement was obtained once the “quasi-stationary” state of the modulated discharge was obtained, several seconds after the ignition of the discharge. In this figure, the shape of the temporal behavior predicted by the theoretical model is also shown.









(b)

