

Collisional Energy Transfer LIF: Using the OH fluorescence for measuring the dissociation of CO₂ in a nanosecond pulsed discharge

M. Ceppelli¹, L.M. Martini^{1*}, M. Scotoni¹, G. Dilecce^{2,1}, P. Tosi^{1,2}

¹Dipartimento di Fisica Università di Trento, Trento, Italy

²P.Las.Mi Lab NANOTEC – CNR, Bari, Italy

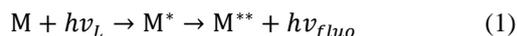
*present address: Department of Applied Physics - Eindhoven University of Technology, The Netherlands

Abstract: Collisional Energy Transfer Laser Induced Fluorescence (CET-LIF), using OH as a probe molecule, can be used for the measurement of simple mixture compositions. Its application to the time-resolved CO₂ dissociation measurement in nanosecond repetitively pulsed (NRP) discharge requires the accurate knowledge of collision rate coefficients in the OH(A, v=0,1) manifold, in conditions of rotational non-equilibrium. Here we report our recent progress on this issue.

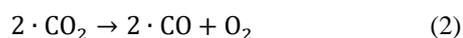
Keywords: Laser-Induced Fluorescence, rate constants, CO₂ conversion.

1. Introduction

In a LIF experiment at atmospheric pressure, the fluorescence $h\nu_{fluo}$ from the excited state M*, prepared by absorption of resonant laser radiation $h\nu_L$,



is strongly influenced by collisions of M* with the surrounding molecules. Since collisions depopulate M* by non-radiative energy-transfer processes, this is a problem for quantitative LIF. However, reversing the point of view, one can imagine using the laser-prepared electronic state M* to probe the environment composition, taking advantage of the fact that collisional energy transfer processes compete with the radiative decay. Thus, changes in the fluorescence outcomes can be related to the variation of the gas composition. Also, assuming that in a CO₂ discharge the dissociation follows the simple scheme



one can express the composition of the gas as a function of the CO₂ conversion, and therefore the latter can be estimated by measuring changes in the gas composition. We have named this method Collisional Energy Transfer CET-LIF and used the OH(A) state as a quantum sensor to measure the time-resolved dissociation of CO₂ in a nanosecond pulsed discharge [1-3].

The knowledge of the rate coefficients for the energy-transfer processes involved is critical for the CET-LIF. However, these processes have been quantitatively well characterised only in conditions of thermal rotational distributions of the OH(A) state, and at $T_{rot}=T_{gas}=300$ K [4]. Such conditions are met in discharge gas mixtures made of buffer He or Ar with only a small addition of molecular gases. In molecular gases, rotational relaxation is far from being complete, and the resulting rotational distributions in the OH(A) manifold are strongly non-

Boltzmann. Due to the significant dependence of collision rate constants on the rotational level, the thermal rate constants measured in [4] cannot be used, and new data are required to quantify the collision processes. To this aim, a new experiment has been set up.

2. Experimental apparatus

The experimental apparatus is shown in Fig. 1. The collision cell is filled with a small amount of vapour from 50% H₂O₂ solution in water and variable amounts of collider gas. The fourth harmonic of an Nd-YAG laser at 266 nm - about 10 mJ/pulse - is used for the production of OH(X) by photo-dissociation of hydrogen peroxide. A second laser beam, at about 281 nm (SH of an Nd-YAG pumped dye laser) pumps the OH(A, v=1) level. Collision rate constants are derived from the LIF pulse temporal decay and the LIF spectrum. Since photo-dissociation

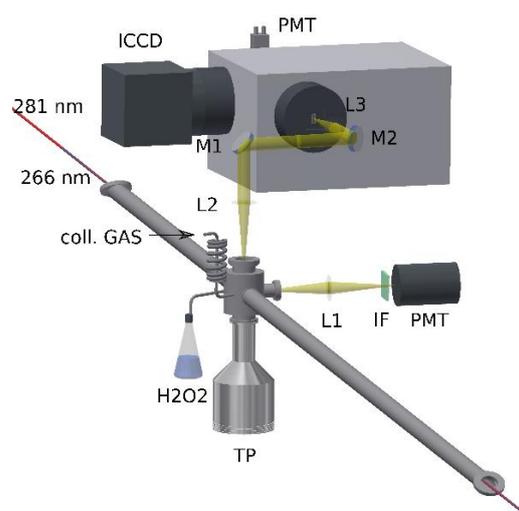


Fig. 1 Drawing of the experimental apparatus. The LIF outcome is measured by a photomultiplier (PMT) for the temporal LIF pulse, and by an ICCD spectrograph for the LIF spectrum.

results in translationally very hot OH(X) fragments, the 281 nm laser beam is fired with a delay of 10 μ s after the 266 nm one, to ensure thermalisation of OH(X). Variation of this delay will eventually allow exploring the kinetic energy dependence of the collision rate constants.

Results

In this communication we shall report results on the values of non-thermal rate constants for quenching and vibrational relaxation with the following colliders: CO₂, O₂, CO, CH₄, H₂ and H₂O. These data are relevant to the use of CET-LIF in dry reforming mixtures since this set of measurements includes initial and final species. The method for retrieving rate coefficients data is the same as that described in [4]. Fluorescence spectra and pulses (see Fig. 2 and 3 for sample measurements) are measured at increasing colliders concentration and analysed to get collision frequencies.

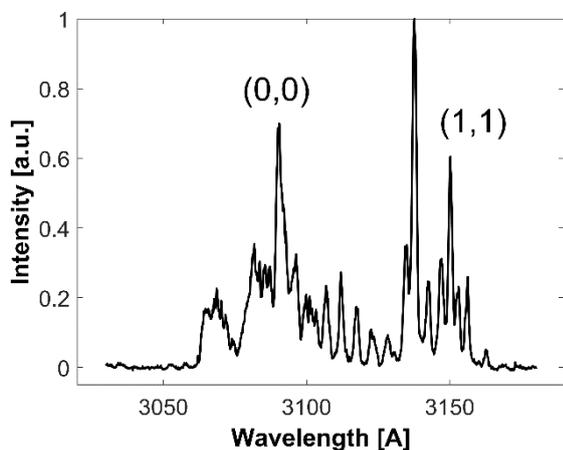


Fig. 2 Fluorescence spectrum at 2.96 mbar CO₂ pressure

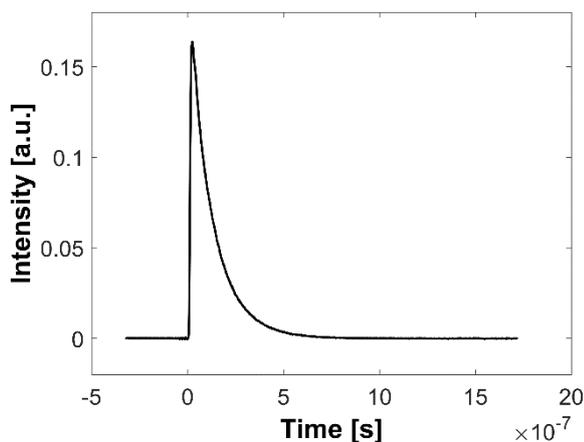


Fig. 3 Fluorescence pulse at 2.96 mbar CO₂ pressure

The frequencies are then plotted as a function of the gas density, obtaining Stern-Volmer plots, as shown in Fig. 4

for the CO₂ case. The slope of the linear fit is the collision rate coefficient. As expected, a marked reduction of the quenching rate coefficient of OH(A,v=0) is observed with respect to the corresponding value at thermal conditions.

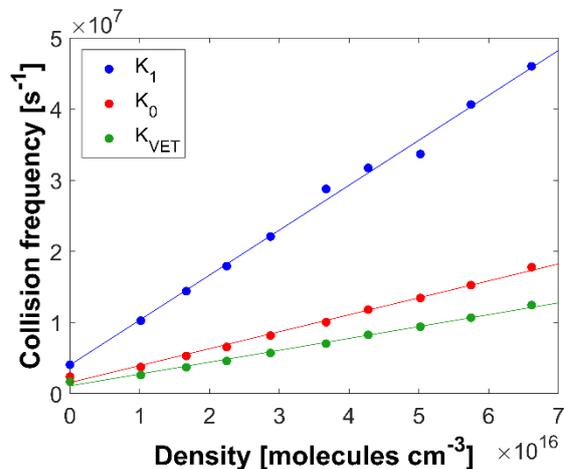


Fig. 4 Stern-Volmer plot of the collision frequency as a function of the density of CO₂ collider.

3. References

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