FEMTOSECOND PUMP-PROBE LIDAR FOR DISCRIMINATING BIOAEROSOLS FROM BACKGROUND URBAN PARTICLES

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ABSTRACT

We present a pump-probe fluorescence depletion scheme enabling to discriminate biological from organic aerosol particles. This new excitation scheme could be useful to further enhance the efficiency of MPEF-LIDAR using the Teramobile.

INTRODUCTION

A major drawback for detecting and identifying bioaerosols using a laser induced fluorescence (LIF)-LIDAR is the presence of organic particles (Diesel particles, soot,..) in the air, which exhibit very similar fluorescence signatures [1,2]. The physical origin of this interference is the excitation in the UV of similar excited states (pi-electrons from benzenic rings) in amino acids (e.g. Tryptophan, Trp) and in PAHs.

We first demonstrated that bioaerosols could be detected by multi-photon excited fluorescence MPEF-LIDAR using the Teramobile. The results show that MPEF-LIDAR is more efficient than standard LIF-LIDAR for distances exceeding a few km.

We now further demonstrated that the major advantage of using a femtosecond LIDAR is the discrimination between bioerosols and background traffic related aerosols. We present a new femtosecond pump-probe depletion (PPD) concept, based on the time-resolved observation of the competition between excited state absorption (ESA) into a higher lying excited state and fluorescence into the ground state. This approach makes use of two physical processes beyond that available in the usual fluorescence spectrum: (1) the dynamics in the intermediate pumped state and (2) the coupling efficiency to a higher lying excited state.

The vibronic excitation relaxes by internal energy redistribution to lower {v'} modes, associated with charge transfer processes (CT), conformational relaxation, and intersystem crossing.

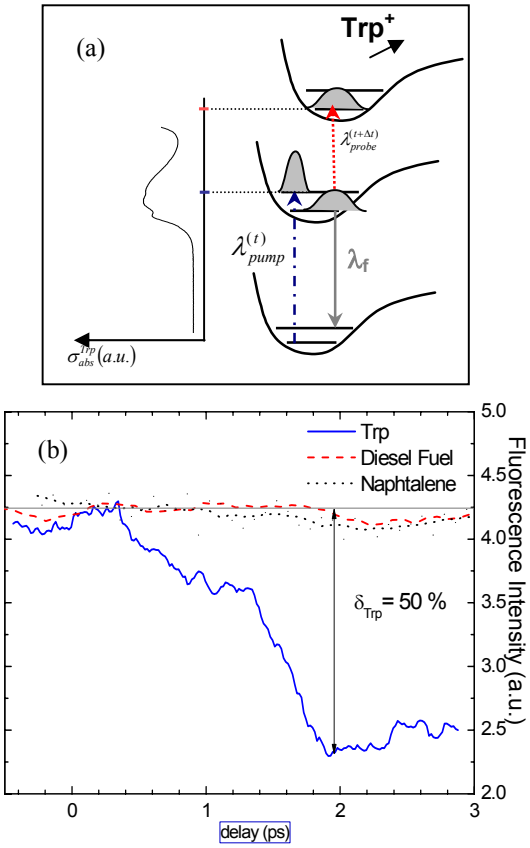

Figure 1. (a)- Pump-probe scheme in the Trp molecule. The pump pulse (at 270 nm) brings molecules to the first Trp excited singlet state. By depleting the fluorescence, the optically delayed probe-pulse moves a portion of the wavepacket into a higher lying excited state (b)- Trp undergoes strong fluorescence depletion (up to 50 %) whereas no significant fluorescence depletion (around 2 %) is observed for Diesel fuel or Naphtalene. The zero delay is arbitrary.

More precisely, in Fig. 1(a) a femtosecond pump pulse (τ=120fs) at 270 nm transfers a fraction of the ground state S0 population of Trp to its S1({v'}) excited state.

After vibronic energy redistribution, fluorescence is emitted from S1({v'}) within a lifetime of 2.6 ns. By illuminating the amino acid with a second pulse (probe) at 800 nm (see Fig. 1b), the S1 population is decreased and the fluorescence depleted.The 800 nm femtosecond laser pulse induces a transition from S1 to an ensemble of higher lying Sn states, which are likely to be autoionizing [3] but also undergo radiationless relaxation into S0 [4]. Fig. 1b shows the fluorescence dependence on the temporal delay between the pump and probe, which depicts the dynamics of the internal energy redistribution within the intermediate excited potential surface S1 of Trp. The same behavior has been observed in live bacteria (*E. Coli*, *B. Subtilis*, *Enterococcus*), showing that Trp-containing proteins undergo the similar relaxation and ionization as pure Trp in water, although their micro-environment significantly differs.

The experiment has been reproduced in organic molecules, representative of transport emissions (naphthalene, diesel fuel): almost no depletion (max. 2 %) was observed (Fig. 1b). We propose to use this striking difference between bio- and non-bio-molecules to distinguish bioaerosols in the air from background urban aerosols. A detection scheme would then consist, in a LIDAR system that sends alternately (a) only the pump pulse and (b) the pump and the delayed probe pulses, and to detect the resulting aerosol fluorescence. By comparing both signals, this technique would be able to distinguish bio-aerosols from organic particles with a contrast of at least 1:25 (50 % depletion for Trp, compared to 2 % for the organic molecules).

This pump-probe two-photon differential fluorescence method will be especially attractive for Lidar, where the lack of discrimination between bioaerosols and transportation related organics is currently most acute. The implementation of the pump-probe technique in a Femtosecond-LIDAR like the Teramobile would lead to the first remote detection system that avoids interference from organic aerosols, (i.e., the first system that could remotely and rapidly detect bacteria in the air under actual urban conditions). Finally, an intriguing question is whether ultrafast pulse shaping of the pump and/or probe pulses could further discriminate between complex bioagents by applying optimization techniques such as Optimal Dynamic Discrimination [7].

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