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Microsecond mid-infrared laser pulses for atmospheric pressure laser ablation/ionization of liquid samples

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ABSTRACT

In many laser based ionization techniques with a subsequent drift time separation, the laser pulse generating the ions is considered as the start time t_0. Therefore, an accurate temporal definition of this event is crucial for the resolution of the experiments. In this contribution, the laser induced plume dynamics of liquids evaporating into atmospheric pressure are visualized for two distinctively different laser pulse widths, $\Delta t = 6$ nanoseconds and $\Delta \tau = 280$ microseconds. For ns-pulses the expansion of the generated vapour against atmospheric pressure is found to lead to turbulences inside the gas phase. This results in spatial and temporal broadening of the nascent clouds. A more equilibrated expansion, without artificial smearing of the temporal resolution can, in contrast, be observed to follow μs-pulse excitation. This leads to the counterintuitive finding that longer laser pulses results in an increased temporal vapour formation definition. To examine if this fume expansion also eventually results in a better definition of ion formation, the nascent vapour plumes were expanded into a linear drift tube ion mobility spectrometer (IMS). This time resolved detection of ion formation corroborates the temporal broadening caused by collisional impeding of the supersonic expansion at atmospheric pressure and the overall better defined ion formation by evaporation with long laser pulses. A direct comparison of the observed results strongly suggests the coexistence of two individual ion formation mechanisms that can be specifically addressed by the use of appropriate laser sources.

1. Introduction

Infrared laser ablation/ionization (IR-LDI) in vacuum and under atmospheric pressure is a well-established analytical technique for direct isolation of charged molecular aggregates of biomolecules. Recently, a special interest towards atmospheric pressure applications has emerged for the direct analysis of native aqueous solutions [1,2]. While in most applications mass spectrometry (MS) is the analyser of choice, IMS is an emerging alternative for rapid screening for known target analytes. The most commonly used IR wavelength is the $\lambda = 2.94$ μm output of Er:YAG lasers or optical parametric oscillators (OPO). This wavelength directly induces excitation in the OH/NH stretch vibration modes of many commonly used solvents including water and alcohols. Its simplicity in term of sample preparation and possibility of coupling to high performance liquid chromatography separation technique makes ambient IR-LDI well suited for a liquid phase on-line analysis with ever increasing significance in real life application [3–5].

Despite the ionization the most fundamental process in any laser ablation based detection is the radiation induced liquid (or solid)-gas phase transition. Though extensive studies on thermal evaporation [6–8], pressure induced phase explosion [9–11] and photoablation [11–14] were performed, the exact involvement of the individual mechanisms remains unclear. The laser irradiation leads to a spontaneous local heating of the sample interrogation volume, the accompanying photoacoustic excitation results in a pressure jump. Both state functions, T and P equilibrate within the sample on timescales governed by the sample material transport properties (thermal conductivity and speed of sound, respectively). Typical values for excitation of water with a focused resonant laser are $\tau_{ac} \sim 1$ ns for acoustic relaxation and $\tau_{th} \sim 1$ μs for thermal equilibration.

The effect of the laser pulse duration with respect to these relaxation rates has been studied by Dreisewerd et al. [15,16] for

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matrix assisted desorption/ionisation (MALDI) in vaccum. According to their observations the nature of IR-LDI is based on the thermal/photo-mechanically induced liquid phase disintegration rather than a pure spallation model previously proposed for vacuum MALDI. The temporal pulse widths studied were 5 ns and 100 ns. For a speed of sound of ~1500 m/s in liquids and a typical penetration depth of several μm these conditions roughly correspond to acoustically confined compared to acoustically unconfined conditions, while thermal confinement was given in both experiments. In vacuum MALDI time of flight (TOF) experiments the pulse width of the ablation/ionization laser defines the temporal (and therefore mass) resolution of the experiment and, thus, has a reasonable upper limit of 100 ns, hence no experiments regarding the effect of thermally unconfined pulses have been conducted.

Modern mass spectrometers coupled to atmospheric pressure exploit a pulsed ion extraction at a continuous sample inlet. In these setups, no upper limit for temporal pulse widths of the used laser is given. In IMS experiments, the experimental resolution is still determined by the temporal definition of the ion formation, however IMS drift times at atmospheric pressure are usually relatively long (several ms) and the resolution of IMS is relatively poor in general when compared to TOF experiments, allowing for the use of microsecond pulse width lasers without affecting the overall resolution of the experiment. Temporal gating of ion flow out of continuous ion sources (like electrospray) has been shown to yield in good resolution utilizing injection times of several hundreds of microseconds [17,18]. Until now the impact of longer pulse duration, in a μs range, on the temporal behaviour of ion formation elucidating the analytical applicability has not been studied. However, such lasers recently became available at affordable prices for tissue ablation and cauterization in medical applications [19].

Despite the laser pulse, the sample itself has been found to play a vital role in determining the exact ablation mechanism [20–24]. The ablation behaviour was found to be strongly depending on the sample's material properties like viscosity, thermal and acoustic conductivity as well as on its shape, temperature and absolute volume [3,12,25–29]. These findings have also been rationalized by the dissipation mechanism of the irradiated energy. At a given material the shape of the sample changes the surface tension distribution, any contact with a substrate or vessel introduces ill-defined boundaries perturbing the thermal and acoustic energy equilibration.

In this work mechanism of laser ablation/ionization of liquid sample at atmospheric pressure is exemplary studied for two distinct pulse widths, $\Delta\tau = 6$ ns and $\Delta\tau = 280$ μs, at a constant wavelength. The chosen pulse widths correspond to the temporal full width at half maximum (FWHM) of the output of a Nd:YAG driven OPO and the output of a diode pumped solid state Er:YAG laser (DPSS). The chosen pulse width of the DPSS laser of 280 μs was empirically found to result in maximum ionization yield. To minimize the introduction of external perturbations by sample handling, the laser ablation was studied on freely hanging droplets.

The two step ablation/ionization dynamics at the two pulse characteristics were studied by interrogating the resulting ion cloud distribution by two orthogonal techniques. In a first experiment, the mere ablation process was visualized by nanosecond resolution high resolution shadowgraphy. In a second experiment the formed ion clouds were guided through an IMS and detected temporally resolved.

2. Methods

For each experiment, a freshly made sample droplet (acetonitrile/water) was dispensed by a syringe pump (KDS 100, KDS Scientific, Holliston, MA, USA). The sample solution was constantly pumped at 20 μL/min into a home-built microdroplet source consisting of a capillary (Hamilton, ID = 110 μm, OD = 235 μm). The fresh surface of each formed sample droplet was intersected by a pulsed laser beam focused by a plano-convex CaF_2 lens (f = 100 mm). In subsequent experiments, two different laser sources were applied, *I)* an OPO (Opotek inc. Carlsbad, CA, USA) with a pulse duration of $\Delta\tau = 6$ ns and *II)* a diode pumped solid state Er:YAG laser (Pantec Engineering AG, Ruggell, Liechtenstein) with a variable pulse duration. Throughout the experiments both lasers were operated resulting in comparable fluences. Deviations in fluences were minimized but could not be avoided due to the differences in the individual lasers beam shape and lasing thresholds. For recording the fluences, the pulse energies were determined with a pyroelectric laser power meter, the sizes of the focal spots were determined as burn spots on photosensitive paper followed by visual inspection under an optical microscope. To have constant thermal lensing in all conducted experiments, both laser systems were operated at a constant repetition rate of 20 Hz.

2.1. Shadowgraphy measurements

For a fast visualization of the evaporation dynamics, back illumination was generated by laser induced fluorescence of methanolic rhodamine B solution (25 μM) placed in a quartz cuvette and excited by the second harmonic of the output of an additional Nd:YAG laser (SpitLight 600, Innolas Laser GmbH, Krailling, Germany). The emitted light pulses were of a temporal width of ~5 ns and, thus allowed to capture high speed shadowgraphy images with nanosecond temporal resolution. The plume was imaged through a macroobjective (Tamron SP 90 mm F/2.8 Di) with adjustable field of vision onto the detector of a Canon EOS digital camera (400D, Canon Inc., Tokyo, Japan). Two delay generators (DG 535, Stanford Research Systems, Sunnyvale, CA, USA) were used to synchronize the triggering of the individual events. The OPO's flashlamp output signal or Er:YAG laser current source output signal, both operating at 20 Hz, were used as master trigger, initiating the chain of subsequent illumination and camera exposure (Fig. 1a)). The camera exposure was triggered via a home-built MOSFET circuit using the remote-control release input of the camera. The microdroplet source described above produced droplets hanging on a metal capillary, providing fresh droplets for reproducible conditions for visualization of subsequent laser ablation processes. All recorded images were post processed for optimal contrast and analysed using the ImageJ software suite (National Institute of Health, USA).

2.2. Ion mobility spectrometry interrogation

The ablated plume was accelerated coaxially into the opening of a home-built liquid injection drift tube IMS consisting of a desolvation cell (1: L = 53 mm, T = 180 °C), connected to a drift tube (2: L = 80 mm, T = 160 °C), *via* a Bradbury-Nielsen type ion grid (3) (Fig. 1b)). The IMS is based on the original design described in [30,31], adopted with a heated gas stream and a desolvation cell as commonly used for liquid sample introduction IMS [32]. Briefly it consists of a tubular arrangement of conductive rings, along which an externally applied electrostatic gradient is realized *via* a series of resistor based voltage dividers. The endcap carries a Faraday plate detector. Along the drift tube separation according to collisional cross section is enhanced by application of a gas stream propagating antiparallel with respect to the electrostatic slope. For an effective transfer of the ablated plume into the IMS a steep voltage gradient was applied: 9.5 kV on the repeller electrode (R), 8.5 kV on the microdroplet source (C) and 7.5 kV on the inlet ring (I). The experiments were conducted in two operating modes: i) by a continuously applied voltage gradient or ii) by pulsed ion extraction