



## Supersonic Jet/Time-of-flight mass spectrometry of adenine using nanosecond and femtosecond lasers

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### Abstract

Mass spectra and ionization efficiencies of adenine were measured with nanosecond (15 ns) and femtosecond (500 fs) laser pulses at identical energy levels. A molecular ion is clearly observed in both spectra, but the efficiency is improved 10-fold when a femtosecond laser is used, indicating the distinct advantage of ultrashort laser pulses for multiphoton ionization of nucleobases in supersonic jet spectrometry.

*Keywords:* Adenine; Ionization efficiencies; Lasers; Mass spectra; Nucleobases

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### 1. Introduction

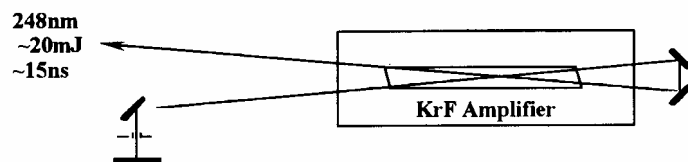
A combination of laser-induced multiphoton ionization (MPI) and time-of-flight (TOF) mass spectrometry (MS) is an extremely useful technique in analytical spectroscopy [1,2]. The supersonic jet technique gives a narrow spectral feature in the ultraviolet and visible spectra and is, therefore, useful for the identification of molecules [3–5]. Such techniques have often been applied to polycyclic aromatic hydrocarbons (PAHs) [6,7] MPI/TOF-MS as well as fluorescence spectrometry

have frequently been used for the detection of molecules. However, nucleobases have seldom been investigated with supersonic jet spectrometry. An examination of the literature reveals that only MPI/MS spectra of uracil, thymine [8], adenine, guanine [9], adenine–thymine and guanine–cytosine [10] have been reported. The reasons for this are obscure but are probably due to poor ionization efficiencies for nucleobases. Picosecond (and nanosecond) laser pulses have been used for efficient MPI in non-jet spectroscopy, e.g. for determination of PAHs with gas chromatographic detection [11]. Recently, femtosecond laser experiments have opened up a new field for examining rearrangements, fragmentations, and dissociations of small molecules when a su-

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## (A) Nanosecond Laser System



## (B) Femtosecond Laser System

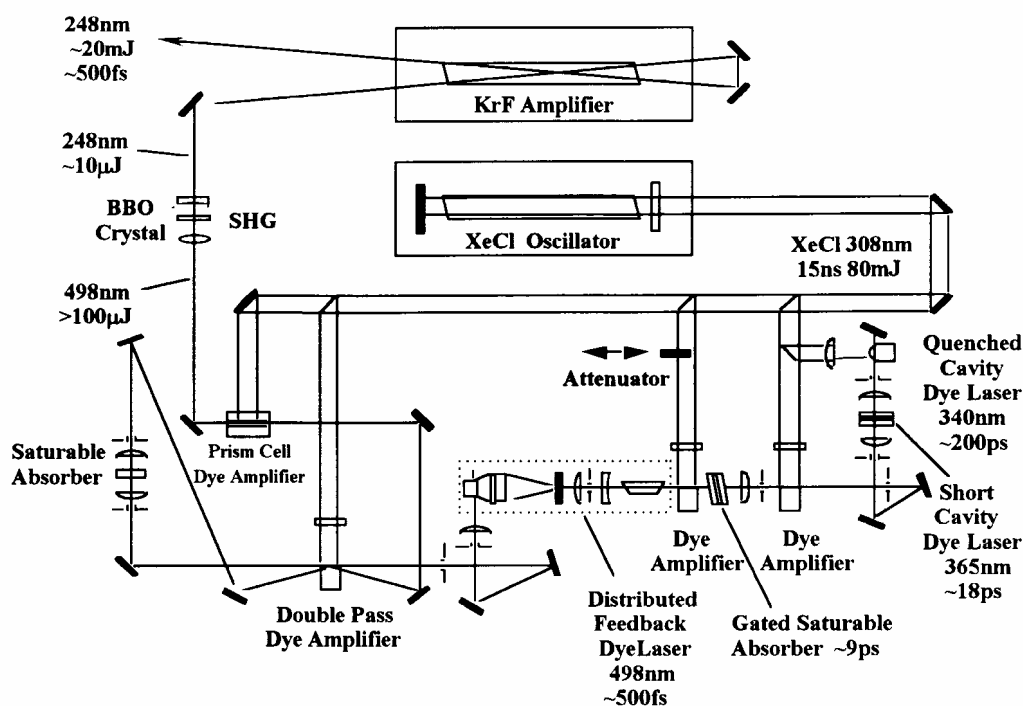


Fig. 1. Laser systems for generation of (A) 15 ns and (B) 500 fs pulses.

personic jet is used [12]. However, no quantitative evaluation of ultrashort laser pulses in analytical spectroscopy has been reported at the time of writing.

In this study, we report MPI/MS of the nucleobase adenine using an ultrashort pulse excimer laser. The mass spectra and ionization efficiencies obtained with nanosecond and femtosecond laser pulses are compared, in order to evaluate the advantages of femtosecond laser ionization in supersonic jet spectrometry.

## 2. Experimental

The experimental set-up comprises a nanosecond/femtosecond laser system and a supersonic jet/TOF mass spectrometer. The supersonic jet spectrometer used in this study has been reported in detail elsewhere [13,14]. The laser is commercially available from Lambda Physik and is only briefly described here. The laser system consists of a dye laser pumped by a XeCl excimer laser, and

a KrF excimer amplifier, as shown in Fig. 1. A quenched-cavity dye laser producing  $\approx 200$  ps pulses [15] is used as a pump source for a short-cavity dye laser to generate  $\approx 9$  ps pulses. After passing it through a gated-saturable absorber [16], the laser beam is then used to pump a distributed-feedback dye laser to generate  $\approx 500$  fs, 0.1 mJ pulses at 496 nm [17,18]. The laser beam is frequency-doubled to 248 nm by a  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO) crystal amplified to 20 mJ by a KrF amplifier. The peak laser power achieved is 40 GW. In contrast, the nanosecond laser pulse is generated by feedback of the amplified spontaneous emission (ASE) through the KrF discharge channel. It produces 15 ns, 10 mJ pulses at 248 nm. A mass spectrum was recorded using a digital oscilloscope (LeCroy 9360), and the signal was averaged 200 times. Adenine, which was used as a sample, was thermally vaporized by elevating the reservoir temperature to 300°C. The laser beam was focused into a supersonic jet using a quartz lens (1 m focal length) and the laser pulse energy was adjusted by passing it through a pinhole. Its value was monitored by a Joule Meter (Molelectron, J3-05DW). Adenine was supplied by Kishida Chemicals (Osaka, Japan).

### 3. Results and discussion

The MPI/TOF mass spectrum was measured by changing the laser pulse energy from 0.02 to 1 mJ using the nanosecond/femtosecond laser. Fig. 2(A) shows the mass spectrum of adenine obtained using 15 ns (80  $\mu$ J) laser pulses. A signal peak at a flight time of 12.4  $\mu$ s corresponds to a molecular ion of adenine ( $m/z$  135), indicating a relatively soft ionization of the molecule. The mass spectrum for adenine has been reported by Li and Lubman [19], using a dye laser emitting at 222 nm, and showed a molecular ion and a fragment ( $m/z$  108, M-HCN). The ionization potential of adenine is approximately 8.48 eV, and the laser wavelength used in this study (248 nm, 5.0 eV) is sufficiently short to allow two-photon ionization. When the laser pulse energy was increased to 1 mJ, the fragment signals (C<sub>1</sub>H<sub>n</sub>, C<sub>2</sub>H<sub>n</sub>, . . . ;  $n = \text{integer}$ ), which are negligibly small in Fig.

2(A), became stronger than the molecular ion signal. Fig. 2(B) shows the mass spectrum obtained using 500 fs (80  $\mu$ J) laser pulses. A strong mass peak corresponding to a molecular ion of adenine (flight time = 12.4  $\mu$ s) is observed. The ionization efficiency is improved to 10-fold in comparison with the spectrum obtained using the nanosecond laser. This signal enhancement is slightly larger than the value obtained for thermally decomposed products of polystyrene (a six-fold increase), where softer ionization was also observed using femtosecond laser pulses [20]. The greater enhancement observed may be due to a faster relaxation rate, i.e. a shorter lifetime in the excited state for adenine in comparison with aromatic hydrocarbons, which result from the thermal decomposition products derived from polystyrene.

The ion signal in the mass spectrum increases with increase in the pulse energy in the experiments using both nanosecond and femtosecond lasers. However, the molecular ion is more efficiently dissociated to small fragments at higher pulse energies. Therefore, it is necessary to optimize the pulse energy to enhance ionization and to minimize photodissociation for sensitive detection of a molecular ion. The relationships between the ionization signals at  $m/z$  135 and the laser

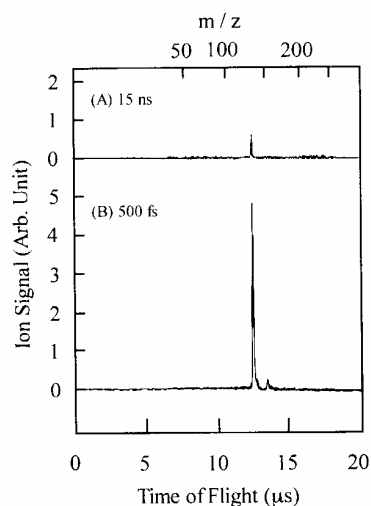


Fig. 2. Mass spectra for adenine, ionized at 248 nm and 80  $\mu$ J, using (A) 15 ns and (B) 500 fs laser pulses.

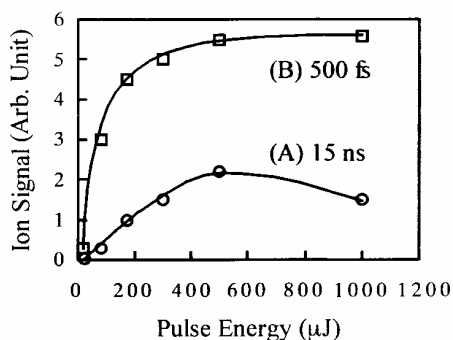


Fig. 3. Dependences of ion signal intensities at  $m/z$  135 on laser pulse energy measured using (A) 15 ns and (B) 500 fs laser pulses. Many fragment peaks and signal peaks occurring from pump oil appear above 1.0 mJ, and so quantitative comparison is difficult above this pulse energy.

pulse energy are shown in Fig. 3. When a nanosecond laser is used, significant photodissociation occurs and the adenine signal decreases above 0.5 mJ. When a femtosecond laser is used, the ionization efficiency is always higher and increases to 1 mJ. This result implies that femtosecond MPI is desired for sensitive detection of a molecular ion.

In preliminary experiments, no signal could be observed for uracil. Two explanations are possible for low ionization efficiencies for nucleobases. First, the ionization potential of uracil might be sufficiently high that the molecule is not ionized using a conventional single-color UV laser. The order of ionization potentials for DNA and RNA bases is uracil (9.32–9.70 eV) > cytosine (8.87–9.43 eV) > thymine (8.68–8.94 eV) > adenine (8.26–8.91 eV) > guanine (7.77–8.30 eV) [21–24]. To overcome this problem, a far-UV laser and/or a two-color MPI scheme might be necessary [8]. The other possibility is that the fast relaxation of energy from the excited state, e.g. intramolecular radiationless transition or photodissociation, occurs before MPI. It is well known that the fluorescence quantum yields are much less for nucleobases, implying shorter lifetimes. Although the relaxation process is not fully understood for biological molecules such as nucleobases, the femtosecond laser may allow faster MPI than intramolecular energy relaxation because of the ultrashort pulse widths. The data presented herein

clearly show that the femtosecond laser is useful for inducing soft ionization of nucleobases and also for a significant improvement in ionization efficiency. The wavelength of the laser is, however, not adjusted to a specific transition, e.g. 0–0 transition. More efficient ionization could be accomplished using a tunable femtosecond laser.

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