

2B15 Decomposition of N-methylaniline and N,N-dimethylaniline in intense laser fields

(Univ. of Tokyo, School of Sci.) ○Peng Liu, Ryuji Itakura, Kaoru Yamanouchi

Introduction

From the series of our recent studies on the behavior of simple aromatic cation molecules in intense fs and ns laser fields by tandem-type time-of-flight (TOF) mass spectrometry [1-4], their decomposition and intra-cluster reaction processes were found to be sensitively dependent on the characteristics of the laser field such as intensity and wavelength. In the present study, the responses of N-methylaniline (NMA) and N,N-dimethylaniline (DMA) to intense ns and fs laser fields are investigated in order to reveal the effect of the methyl group substitution on the fragmentation and decomposition processes of the aniline moiety.

Experiment

The vapor of NMA or DMA sample gas seeded in He expands into the vacuum chamber through a pulsed valve with the stagnation pressure of 1 atm and is skimmed by a skimmer. The fourth harmonics (266 nm) of Nd:YAG laser light crossing with the collimated molecular beam at right angles is focused on the molecular beam to produce the parent ions through multiphoton ionization. The fragment ions are also produced at the photoionization stage, but only the parent ions are allowed to pass through the first stage of the tandem-type time-of-flight (TOF) mass spectrometer equipped with a mass gate. The parent ions are irradiated with the intense femto second (fs) laser field ($\lambda = 395$ nm, $\Delta t = 50$ fs, $I \sim 10^{16}$ W/cm²) or with the nano second (ns) laser field ($\lambda = 532$ nm, $\Delta t = 6$ fs, $I \sim 10^{10}$ W/cm²), and the resultant fragment cations are mass-selected in the second stage of the tandem-type TOF mass spectrometer, and are detected by a MCP detector.

Results and discussion

In Fig.1(a), the TOF mass spectrum is obtained when NMA⁺ is irradiated with the intense fs laser light. The major peaks are assigned to C₆H₅N⁺, C₆H₅⁺, C₅H₅⁺, C₄H₃⁺, and C₃H₃⁺. Among them C₆H₅⁺ has the largest yield, indicating that the breaking of the C-N bond, C₆H₅NHCH₃⁺ → C₆H₅⁺ + NHCH₃, is the dominant channel. In the ns laser case, basically the same ion species are seen in the TOF mass spectrum as shown in Fig.1(b). It can be noticed that the yield of C₄H₃⁺ is the largest among the smaller ion species than C₆H₅⁺. When the laser field intensity is increased from 0.15×10^{10} W/cm² to 1.38×10^{10} W/cm², the relative yield of C₆H₅⁺ decreases from 76.2% to 52.2% monotonically, while that of C₄H₃⁺ increases from 4.0% to 21.9%, and C₃H₃⁺ increases from 2.1% to 6.3%. It is noteworthy that the sum of the yields of these three fragment ion species is kept almost constant at 80~82 % in the entire range of the laser field intensity, and that the yield of C₅H₅⁺ (~15%) is almost unchanged. This indicates that C₆H₅⁺ produced in the low laser-field intensity regime as one of the nascent fragment ion species absorbs more photons and decomposes into C₄H₃⁺ and C₃H₃⁺, while C₅H₅⁺ does not absorb additional photons. Considering this laser-field intensity dependence,

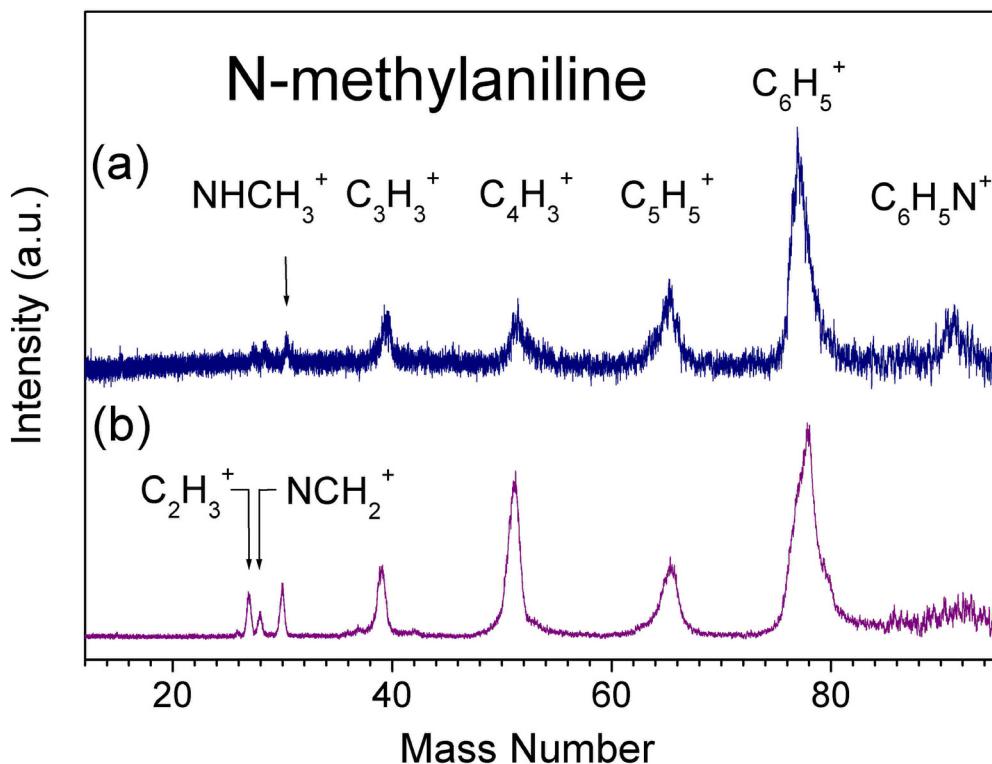


Fig 1. Decomposition of N-methylaniline in (a) fs laser field (1.0×10^{16} W/cm 2) and (b) ns laser field (1.4×10^{10} W/cm 2).

the larger yield of C_6H_5^+ in the fs laser field may be interpreted in a way that the temporal duration of the laser field is too short for the nascent C_6H_5^+ to absorb the energy from the light field.

The fragmentation patterns of DMA $^+$ in the fs and ns laser fields were found to be similar to those of NMA $^+$ except for the appearance of $\text{C}_6\text{H}_5\text{NCH}^+$. In the fs laser field, C_5H_4^+ and C_5H_3^+ were observed in addition to C_5H_5^+ , but C_5H_4^+ and C_5H_3^+ were not produced in the ns laser field, suggesting that C_5H_4^+ and C_5H_3^+ , which are more unsaturated than C_5H_5^+ , could absorb additional photons more efficiently. The mechanism of the formation of the five-member ring cations is discussed by referring to the decomposition process of aniline cations and aniline ammonia cluster cations.

References

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