Decomposition of N-methylaniline and N,N-dimethylaniline in intense laser fields
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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 femtosecond (fs) laser field (λ = 395 nm, ∆t = 50 fs, I ∼ 10^{16} W/cm²) or with the nano second (ns) laser field (λ = 532 nm, ∆t = 6 fs, I ∼ 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 C_6H_5N^+, C_6H_5^+, C_5H_5^+, C_4H_3^+, and C_3H_3^+. Among them C_6H_5^+ has the largest yield, indicating that the breaking of the C-N bond, C_6H_5NHCH_3^+ → C_6H_5^+ + NHCH_3, 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 C_4H_3^+ is the largest among the smaller ion species than C_6H_5^+. 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 C_6H_5^+ decreases from 76.2% to 52.2% monotonically, while that of C_4H_3^+ increases from 4.0% to 21.9%, and C_3H_3^+ 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 C_5H_5^+ (~15%) is almost unchanged. This indicates that C_6H_5^+ produced in the low laser-field intensity regime as one of the nascent fragment ion species absorbs more photons and decomposes into C_4H_3^+ and C_3H_3^+, while C_5H_3^+ does not absorb additional photons. Considering this laser-field intensity dependence,
the larger yield of $\text{C}_6\text{H}_5^+$ 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 $\text{C}_6\text{H}_5^+$ 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 $\text{C}_6\text{H}_5\text{NCH}_2^+$. In the fs laser field, $\text{C}_5\text{H}_4^+$ and $\text{C}_5\text{H}_3^+$ were observed in addition to $\text{C}_5\text{H}_5^+$, but $\text{C}_5\text{H}_4^+$ and $\text{C}_5\text{H}_3^+$ were not produced in the ns laser field, suggesting that $\text{C}_5\text{H}_4^+$ and $\text{C}_5\text{H}_3^+$, which are more unsaturated than $\text{C}_6\text{H}_5^+$, 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