Multiphoton Ionization Detection of Aromatic Hydrocarbons at 157.6 nm

Nozomu Kanno,[1] Akihiro Yabushita,[2] Masahiro Kawasaki,[3] and Kenichi Tonokura*[1]
[1]*Environmental Science Center, The University of Tokyo, Tokyo 113-0033*
[2]*Horiba Ltd., Kyoto 601-8510*
[3]*Department of Molecular Engineering, Kyoto University, Kyoto 615-8510*

(Received November 10, 2006; CL-061323; E-mail: tonokura@esc.u-tokyo.ac.jp)

Multiphoton ionization at 157.6 nm using F_2 laser has been used for the detection of benzene, toluene, and chlorobenzene. In all the photoionization spectra, the fragment ion signal intensities were stronger than those of the molecular ions. The detection limits of the compounds are discussed in terms of the multiphoton ionization schemes of the compounds.

Aromatic hydrocarbons are important components of automobile tailpipe exhaust and evaporative emissions and contribute to the formation of ozone and secondary organic aerosols in urban air. In addition, aromatics such as benzene, toluene, and chlorobenzene are causative agents for sick building syndrome. Multiphoton ionization (MPI) at around 260 nm and single-photon ionization (SPI) at 118 nm have been widely used for the detection of aromatic hydrocarbons, with sufficient detection sensitivity.[1–5] In MPI schemes of aromatic compounds, electronically and vibrationally excited states affect the mass spectral pattern and hence the detection sensitivity.[6–10] In this paper, we have demonstrated the detection of benzene, toluene, and chlorobenzene using time-of-flight (TOF) mass spectrometry coupled with MPI at 157.6 nm. The detection limits of these species were determined and are discussed from the perspective of their MPI schemes.

The apparatus consists of a sample inlet system connected to a TOF mass spectrometer. The mass spectrometer can be operated as a Wiley–McLaren type.[11] An effusive molecular beam was introduced into the TOF mass spectrometer. Ionization was accomplished by MPI at 157.6 nm (7.87 eV). An MgF_2 lens with a focal length of 20 cm was used to focus the F_2 laser output (Lambda Physik, Optex Pro) at 157.6 nm with a maximum power of 1 mJ pulse^{-1}. The laser power was monitored using a solar blind phototube (Hamamatsu R1132). The laser was operated at 20 Hz. The diluted gas mixture of 10-ppm benzene/10-ppm toluene/10-ppm chlorobenzene in N_2 was purchased from Takachiho Co. The premixed sample gases diluted by He or N_2 buffer gases were prepared from liquid samples and then used to measure the ionization mass spectra and the detection limits.

Figure 1 shows the MPI spectra of benzene, toluene, and chlorobenzene. These ionization spectra are different from those measured by SPI at 118 nm[5] and by electron impact ionization at 70 eV.[12] In the ionization spectrum of benzene (Figure 1a), $C_6H_n^+$, $C_4H_n^+$, and $C_3H_n^+$ fragment ion signals were observed. The largest signal was $C_4H_4^+$ ($m/z = 52$). In the case of toluene (Figure 1b), more than half of the total ions detected were $C_7H_7^+$ ($m/z = 91$), and the second major ion signal was $C_3H_3^+$ ($m/z = 39$). In the mass spectrum of chlorobenzene (Figure 1c), $C_6H_5^+$ ($m/z = 77$), and $C_4H_n^+$ were measured as major ion signals.

The power dependence of each parent molecular ion signal corresponds to a two-photon process, whereas fragment ion signals appeared via three- to seven-photon processes, indicating excitation energies up to 55 eV. In the cases of the most abundant fragment signals for benzene ($m/z = 52$), toluene ($m/z = 91$), and chlorobenzene ($m/z = 77$), the estimated photon numbers absorbed in the ionization process were 4.4 ± 0.4, 4.4 ± 0.5, and 3.7 ± 0.4, respectively. The orders of laser power dependency of the total ion signals of benzene, toluene, and chlorobenzene were 3.9 ± 0.5, 4.3 ± 0.4, and 3.3 ± 0.5, respectively. Although each fragmentation process seems to be quite complicated, the ionization efficiencies of these species would be described by three- or four-photon schemes.

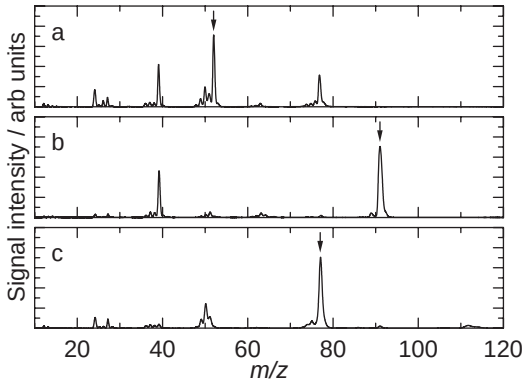


Figure 1. Multiphoton ionization mass spectra of (a) benzene, (b) toluene, and (c) chlorobenzene at 157.6 nm. All reagents were diluted to 0.1% in He. Arrows indicate the peaks used for estimating the detection limits.

The detection limits for obtaining signal to noise (S/N) ratios of 2 for benzene, toluene, and chlorobenzene were estimated at the largest ion signals, $m/z = 52$, 91, and 77, respectively. A series of measurements using calibration gases were performed to obtain calibration curves and sensitivity limits for the aromatic compounds. Figure 2 shows ion signal intensity versus sample gas mixing ratio plots. The measurement time for each point in Figure 2 was 50 s. The plots show good linear relationships over the wide dynamic range of four orders of magnitude. Detection limits with S/N = 2 for benzene, toluene, and chlorobenzene are around 230, 9.4, and 580 ppbv, respectively. Mühlberger et al. measured SPI spectra of benzene, toluene, and chlorobenzene at 118 nm and determined the detection limits at 10 s measurements to be 1.5, 2, and 7 ppbv.[2] They also determined the detection limits of benzene and toluene in the 259-nm MPI to be a few ppbv. For toluene, the detection limits for the 157.6-nm MPI, the 118-nm SPI, and the 259-nm MPI were in the same order of magnitude. In the MPI at 157.6 nm, the detection limit of toluene was 20 times smaller than that of benzene.

The reported absorption coefficients of benzene and toluene at 157.6 nm were almost the same, 1.9 and 1.8×10^{-17}

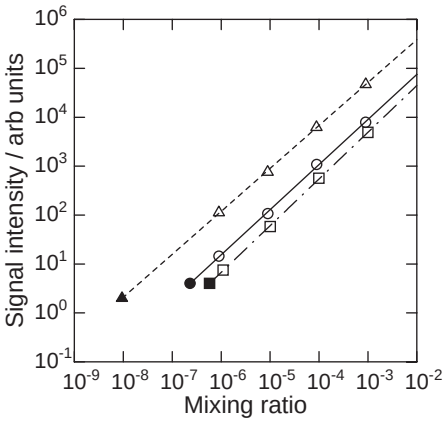
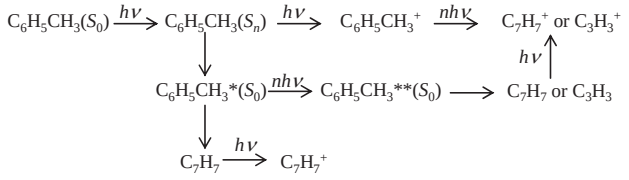


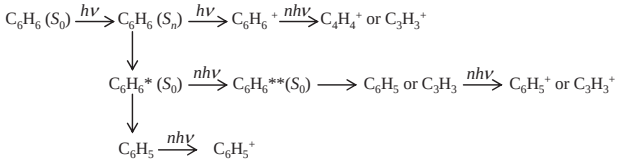
Figure 2. Concentration dependences of $C_4H_4^+$ from benzene (open circles), $C_7H_7^+$ from toluene (open triangles), and $C_6H_5^+$ from chlorobenzene (open boxes). Solid symbols denote the detection limits for S/N = 2.

cm^2 $molecule^{-1}$.[13] Kimura and Nagakura measured absorption spectra of benzene, toluene, and chlorobenzene in the range of 160 to 220 nm.[14] Extrapolating their spectra to 157.6 nm, the absorption cross sections of these three species are expected to be roughly the same. These results indicate that the primary absorption efficiencies of benzene, toluene, and chlorobenzene would be roughly the same. For benzene and toluene, the primary excited molecules rapidly form hot molecules, i.e., vibrationally excited molecules in the ground electronic state. In the RRKM theory, Kislov et al. calculated that the photodissociation rate of hot benzene at 157.6 nm to be 3.48×10^7 s^{-1}, corresponding to the lifetime of 29 ns.[9] They also predicted that 97.5% of hot benzene excited at 157.6 nm dissociates to C_6H_5. The ionization energy of C_6H_5 was estimated to be 8.32 ± 0.04 eV, which was larger than the 7.87 eV of the 157.6-nm photon energy.[15] In the case of toluene, Shimada et al. observed benzyl radicals produced from the photodissociation at 157.6 nm and estimated the dissociation rate to be $(9.3 \pm 0.7) \times 10^7$ s^{-1}, which corresponds to the lifetime of 11 ns.[7] Luther et al. measured the branching ratio of the C–C and C–H bond splits of toluene at 193 nm.[6] They estimated the internal energy dependence based on the statistical adiabatic channel model. The estimated yields of the benzyl radical formation were 0.75 and 0.71 at 60,000 and 70,000 cm^{-1}, thus the interpolated value at 157.6-nm excitation is 0.73. The ionization energy of the benzyl radical was estimated to be 7.242 ± 0.006,[12] lower than the 157.6-nm photon energy (7.87 eV). The lower detection limit of toluene would be caused by the efficient ionization from the benzyl radical (Schemes 1 and 2).

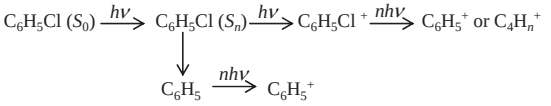
In the MPI of benzene at 193 nm, Mori and Kitagawa suggested that the $C_4H_4^+$ ion was produced mainly from the excited $C_6H_6^+$ ion.[8] In the case of chlorobenzene, Kadi et al. estimated



Scheme 1.



Scheme 2.



Scheme 3.

the excited state lifetime at 266-nm excitation to be 1 ns, assigned to the decay of the initially excited (π, π^*) singlet state to the repulsive (n, σ^*) triplet state due to spin–orbit coupling.[10] The formation of excited $C_6H_5Cl^+$ in the multiphoton process would be retarded by the extremely short lifetime in the electronically excited state of chlorobenzene. The weak intensity of the $C_4H_4^+$ signal from chlorobenzene can be explained by the short lifetime of the excited state of chlorobenzene. This also affects the lower detection sensitivity of chlorobenzene (Scheme 3).

In the proposed ionization scheme, the parent ions in the 157.6-nm MPI are produced in the two photon process. On the other hand, the fragment ions are produced in the MPI process more than three photons, which consist with the laser power dependences.

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