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メタデータ	言語: English 出版者: Chemical Society of Japan 公開日: 2019-05-28 キーワード (Ja): キーワード (En): ionization potential, solvation, sub-nanosecond visible laser 作成者: 大矢, 直樹, ハッ橋, 知幸 メールアドレス: 所属: Osaka City University, Osaka City University
URL	<a href="https://ocu-omu.repo.nii.ac.jp/records/2019743">https://ocu-omu.repo.nii.ac.jp/records/2019743</a>

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<b>Citation</b>	Chemistry Letters, 47(8); 1014-1017
<b>Issue Date</b>	2018-07-21
<b>Type</b>	Journal Article
<b>Textversion</b>	author
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<b>DOI</b>	10.1246/cl.180379

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# Eluent-assisted Nonresonant Multiphoton Ionization of Polycyclic Aromatic Hydrocarbons in a Liquid Chromatograph-Mass Spectrometer

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1 A sub-nanosecond visible laser coupled with a liquid  
2 chromatograph is utilized for atmospheric pressure laser  
3 ionization (APLI). We reveal that the range of applicable  
4 substances for nonresonant three-photon ionization is  
5 determined by the proton affinity and the ionization  
6 potential, the latter of which is lowered by solvation with  
7 eluents. APLI with a visible laser can be used for  
8 fragmentation- and background-free detection of analytes as  
9 well as to investigate the ionization threshold of solvated  
10 molecules.

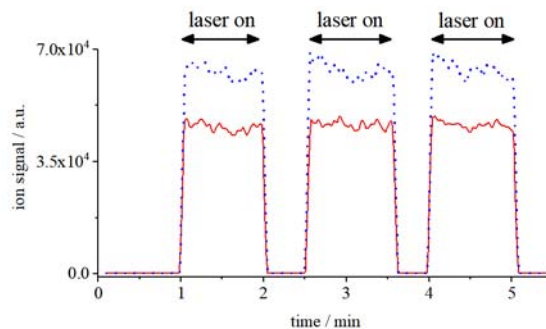
11 **Keywords:** ionization potential, solvation, sub-  
12 nanosecond visible laser

13 Polycyclic aromatic hydrocarbons (PAHs) are regarded  
14 as environmental pollutants,<sup>1</sup> and some of them are  
15 mutagenic and carcinogenic.<sup>2</sup> A gas chromatograph<sup>3</sup> or  
16 liquid chromatograph,<sup>4</sup> coupled with an atmospheric  
17 pressure ionization mass spectrometer, in which mass  
18 spectrometry is performed by ionizing analytes in an  
19 atmospheric pressure environment, is commonly used to  
20 analyze PAHs. Several ionization methods that can be used  
21 under atmospheric pressure have been developed:  
22 atmospheric pressure chemical ionization (APCI),<sup>5</sup>  
23 atmospheric pressure photoionization (APPI),<sup>6,7</sup> and  
24 atmospheric pressure laser ionization (APLI).<sup>8</sup> APCI ionizes  
25 an eluent by corona discharges, and the proton transfer from  
26 eluent cations to analytes enables the detection of  
27 protonated analytes.<sup>5</sup> In the case of APPI, the VUV light  
28 (>10 eV) emitted from a rare gas lamp ionizes analytes by a  
29 single-photon absorption process.<sup>6,7</sup> APLI has made  
30 significant improvements in detection limits by utilizing the  
31 resonance-enhanced multiphoton ionization (REMPI)  
32 process, in which the two-photon ionization is enhanced  
33 when the first transition is resonant with an electronically  
34 excited state. In APLI, a UV photon emitted from a  
35 nanosecond excimer laser is commonly used. The typical  
36 wavelength, pulse duration, and repetition rate for an  
37 excimer laser used in APLI are 248 nm (4.99 eV), 5–10 ns,  
38 and 100–200 Hz, respectively. In some cases, a compact  
39 nanosecond UV laser<sup>9</sup> or picosecond UV laser<sup>10</sup> has been  
40 applied for APLI. APLI has been used successfully for the  
41 detection of a variety of molecules, but the reduction of  
42 ionization potential of analytes (<1 eV) in eluents cannot be  
43 investigated because sufficiently high energy for ionization  
44 is deposited by ultraviolet light. In order to investigate the  
45 ionization threshold of solvated molecules, a low-energy  
46 photon must be used for the ionization. As a consequence,  
47 short duration but narrow spectral width laser pulses are  
48 required for nonresonant multiphoton ionization.

49 In this study, we utilized a compact, high-repetition (1  
50 kHz), visible (532 nm, 2.33 eV) laser with a 500 ps duration

51 attached without modification to a conventional liquid  
52 chromatograph-mass spectrometer (LC-MS) for APLI. The  
53 experimental details are described in the Supporting  
54 Information. Anthracene was chosen as a typical PAH to  
55 investigate the ion signal variations depending on the  
56 parameters of the MS as well as the laser power. We also  
57 discussed the applicability for various PAHs. The results  
58 obtained by APLI were compared with those obtained by  
59 APCI. We reveal that the nonresonant multiphoton  
60 ionization of PAHs is possible due to the lowering of  
61 ionization potential by the solvation with eluents.

62 Figure 1 shows the selected-ion monitoring  
63 chromatogram of anthracene obtained by APLI. Anthracene  
64 methanol (MeOH) solution was directly injected into the  
65 MS (DI-MS) by a syringe pump. The results clearly showed  
66 that both the molecular cation radical ( $M^{+\bullet}$ ) and protonated  
67 molecule ( $MH^+$ ) appeared only when the laser beam was  
68 irradiated.

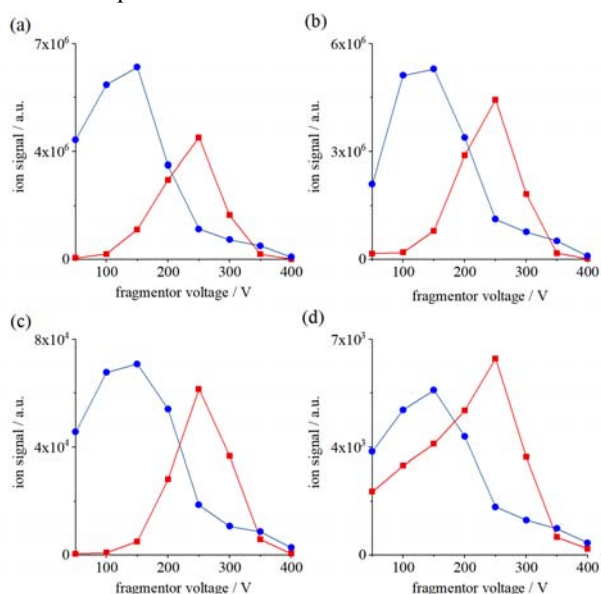


69

70 **Figure 1.** Selected-ion monitoring chromatogram of anthracene (300  
71 ppm) measured by DI-MS (solid line,  $M^+$ ,  $m/z=178$ , fragmentor  
72 voltage = 240 V; dotted line,  $MH^+$ ,  $m/z=179$ , fragmentor voltage = 120  
73 V). Methanol was used as an eluent. Laser power was 42 mW. The  
74 arrows indicate the duration when the laser is irradiated.

75 We then varied the fragmentor voltage to clarify  
76 whether the primary ion of anthracene is  $M^{+\bullet}$  or  $MH^+$ . The  
77 formation of  $M^{+\bullet}$  from  $MH^+$  by the collisions with residual  
78 nitrogen gases in MS is enhanced when the fragmentor  
79 (acceleration) voltage increases. Thus, the primary ion is  
80 expected to be identified under low fragmentor voltage  
81 conditions. Anthracene solution was injected into the MS  
82 via the LC by using MeOH or acetonitrile (MeCN) as an  
83 eluent. Figures 2a and 2b clearly show that the primary ion  
84 of anthracene formed by APCI was  $MH^+$  in both MeOH and  
85 MeCN. The same result was obtained for APLI when  
86 MeOH was used as an eluent (Figure 2c). In contrast, the  
87 abundant formation of  $M^{+\bullet}$  was observed even at low  
88 fragmentor voltage when MeCN was used as an eluent in  
89 the case of APLI (Figure 2d). These differences are

1 attributed to the different primary ion formation processes.  
 2 APCI mainly ionizes eluents by corona discharges followed  
 3 by the proton transfer to the analyte. Protonation of  
 4 anthracene is an exothermic process in both MeCN and  
 5 MeOH because the proton affinity (PA) of anthracene (9.01  
 6 eV)<sup>11</sup> is higher than that of MeOH (7.82 eV) or MeCN (8.08  
 7 eV).<sup>12</sup> In contrast, anthracene is preferentially ionized to  
 8 form  $M^{++}$  by APLI, since the ionization potential (IP) of  
 9 anthracene (7.43 eV) is much lower than those of the  
 10 eluents: 10.85 eV for MeOH; 12.19 eV for MeCN.<sup>13</sup> In the  
 11 case of APLI, the successive abstraction of hydrogen from  
 12 the eluent by  $M^{++}$  forms the secondary ion  $MH^+$ . It is also  
 13 safe to say that the hydrogen abstraction is less efficient in  
 14 MeCN than in MeOH.<sup>14</sup> Therefore, both  $M^{++}$  and  $MH^+$  are  
 15 detected in MeCN, but only  $MH^+$  is detected in MeOH at  
 16 low fragmentor voltage in the cases of APLI. More  
 17 importantly, the ion signal obtained by APLI in MeOH was  
 18 about one order of magnitude larger than that in MeCN,  
 19 while the ion signals obtained by APCI in both MeOH and  
 20 MeCN were on the same order of magnitude. The ionization  
 21 potential of anthracene in MeOH is lower than that in  
 22 MeCN.<sup>15</sup> Therefore, the amount of  $M^{++}$  produced by APLI in  
 23 MeOH may be larger than that in MeCN as the efficiency of  
 24 ion production by the multiphoton process is strongly  
 25 dependent on the ionization potential. In the cases of APCI,  
 26 the amount of  $MH^+$  obtained in MeOH is expected to be  
 27 similar to that obtained in MeCN because the transfer of  
 28 proton that is produced by corona discharges of eluents is an  
 29 exothermic process in both MeOH and MeCN.



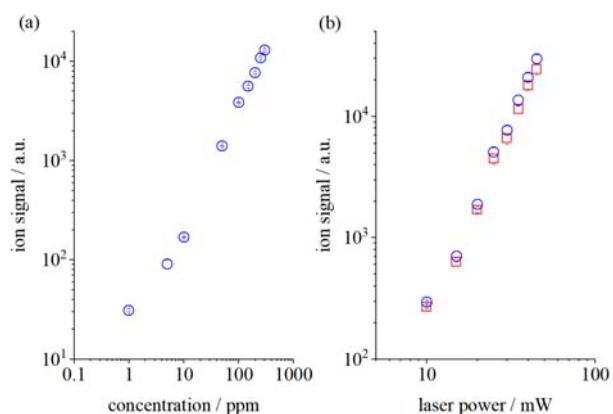
30  
 31 **Figure 2.** The correlations between ion signals of anthracene (triangles,  
 32  $M^+$ ,  $m/z=178$ ; circles,  $MH^+$ ,  $m/z=179$ ; squares, the sum of  $M^+$  and  
 33  $MH^+$ ) and fragmentor voltages. Anthracene was analyzed by APCI (a,  
 34 b) or APLI (c, d). MeOH (a, c) or MeCN (b, d) were used as eluents.

35 Having clarified the origin of  $M^{++}$  and  $MH^+$ , we next  
 36 focused on other ions produced by APCI and APLI. The  
 37 mass spectra of anthracene obtained by APCI (Figure S2a)  
 38 included ions that originated from anthracene, eluent, and

39 presumably impurities, while that obtained by APLI (Figure  
 40 S2b) included only the ions of anthracene. The  
 41 fragmentation- and background-free features of APLI<sup>8,16</sup>  
 42 were also confirmed with a sub-nanosecond visible laser.

43 We confirmed that the ion signal was linearly  
 44 proportional to the concentration of anthracene in MeOH  
 45 (Figure 3a,  $r^2 = 0.996$ , 1–300 ppm). Since the laser power  
 46 was stable enough during the experiments, the fluctuation of  
 47 the ion signal was satisfactorily small. However, the limit of  
 48 detection was far from that achieved by the established  
 49 APLI methods<sup>8,16</sup> applied for real environmental samples.  
 50 For example, the limit of detection of PAHs achieved by  
 51 APLI with a time-of-flight MS was on the order of tens of  
 52 femtograms.<sup>16</sup> The unfavorable detection limit of the present  
 53 results was attributed to the very small volume of primary  
 54 ionization as well as the small cross section of multiphoton  
 55 ionization. We must focus the laser beam to reach the high  
 56 intensity required for induction of the multiphoton  
 57 absorption process, whereas the sample and eluent from LC  
 58 are nebulized in a heated tube and then spread out orders of  
 59 magnitude wider than the focus of the laser beam. Therefore,  
 60 only a small part of the sample vapor is exposed to a  
 61 focused laser beam. Though the limit of detection is not  
 62 within the scope of this study, we might suggest that this  
 63 limitation would be improved by increasing the peak laser  
 64 power and ionization volume as well as by using a time-of-  
 65 flight MS instead of the quadrupole MS used in this study.

66 Ionization of anthracene by sub-nanosecond visible  
 67 laser pulses occurred definitively by the multiphoton  
 68 process because the signals of both  $M^{++}$  and  $MH^+$   
 69 were nearly proportional to the cube of the laser power (Figure 3b,  
 70 MeOH). A least square fitting of data gives the slopes of  
 71 3.12 ( $M^{++}$ ) and 3.19 ( $MH^+$ ), respectively. However, the  
 72 energy of three 532 nm photons (6.99 eV) is insufficient to  
 73 ionize anthracene in the gas phase.

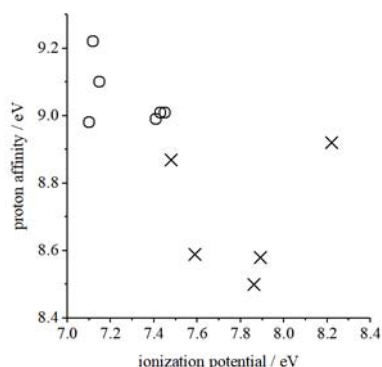


74  
 75 **Figure 3.** The correlation between ion signals (circles,  $MH^+$ ,  $m/z=179$ ,  
 76 fragmentor voltage = 120 V; squares,  $M^+$ ,  $m/z=178$ , fragmentor  
 77 voltage = 240 V) measured by APLI and (a) the concentration of  
 78 anthracene or (b) laser power. The ions were measured by (a) LC-MS  
 79 and (b) DI-MS. The vertical bars in (a) give the standard deviation  
 80 obtained in the three measurements. MeOH was used as an eluent.

81 We can suggest three possible ionization mechanisms.  
 82 First, the three-photon ionization process is possible if the

1 ionization potential of anthracene in the solvated form is  
 2 sufficiently lower than that in the isolated form. The  
 3 ionization potentials of anthracene solids have been reported  
 4 to be 5.70 (bulk) and 6.4 eV (near to the surface),  
 5 respectively.<sup>17</sup> It is known that the vertical ionization  
 6 potential of metals and molecules decreases by clustering  
 7 with polar molecules.<sup>18</sup> By analogy to those findings, a  
 8 reduction in the ionization potential to 6.99 eV by  
 9 polarization effects is expected for solvated anthracene.<sup>15</sup>  
 10 The second possible explanation is that  $M^{+}$  is formed by the  
 11 3+1 REMPI process, in which ionization occurs via the  
 12 excited state of PAHs, which is reached by the three-photon  
 13 absorption process. Due to the high density of states in such  
 14 high-energy regions, the transition to a continuum level by  
 15 an additional 532 nm photon absorption may be allowed.  
 16 Assuming that this single-photon allowed transition occurs,  
 17 the slope obtained by the power-dependence experiments  
 18 would reflect the rate-limiting three-photon absorption  
 19 process. However, the 3+1 REMPI process is unlikely,  
 20 because the lifetime of highly excited states is extremely  
 21 short (<0.1 ps).<sup>19</sup> Third, the absorption of four 532 nm  
 22 photons, equivalent to 9.32 eV, which well exceeds the  
 23 ionization threshold of anthracene in the gas phase, could be  
 24 suggested. The discrepancy between the experimentally  
 25 obtained slopes (3.1) and the number of photons required by  
 26 the energy conservation law (4) is presumably explainable  
 27 by the volume effect.<sup>21</sup> The expansion of ions that formed at  
 28 the most tightly focused volume before detection by MS  
 29 appears to be responsible for making the slope in Figure 3b  
 30 less steep than expected.

31 Although we can suggest the three possible ionization  
 32 mechanisms above, we cannot state which mechanism is  
 33 operative based only on the results for anthracene. Therefore,  
 34 we analyzed a variety of PAHs (50 ppm) by the scan mode  
 35 ( $m/z = 50-300$ ) of LC-MS to explore the applicability of  
 36 APLI with a sub-nanosecond visible laser. Table S1 shows  
 37 the properties of PAHs as well as the relative abundance of  
 38 ions detected by APLI or APCI. We detected 7 out of the 13  
 39 PAHs by APLI. The detected PAHs were anthracene,  
 40 pyrene, benzo[a]anthracene, benzo[a]pyrene,  
 41 dibenz[a,h]anthracene, benzo[g,h,i]perylene, and  
 42 indeno[1,2,3-c,d]pyrene. In the case of APCI,  
 43 benzo[k]fluoranthene was also detected. This result  
 44 indicates that the performance of APLI using a sub-  
 45 nanosecond visible laser is similar to that of APCI, at least  
 46 for the selected PAHs.



48 **Figure 4.** Correlation between the proton affinity and ionization  
 49 potential of PAHs in the gas phase. Circles and crosses indicate that  
 50 PAHs were detected and not detected by APLI, respectively. MeOH was  
 51 used as an eluent.

52 Figure 4 shows the correlation between PAs and IPs of  
 53 11 PAHs whose IPs and PAs are known or estimated. The  
 54 PAHs detected by APLI are indicated by circles. Those not  
 55 detected by APLI are indicated by crosses. The largest  
 56 signal obtained by both APCI and APLI was that for  
 57 benzo[a]pyrene, which had the second smallest IP and the  
 58 largest PA among the 11 PAHs. The quantitative arguments  
 59 about the amount of ion cannot be made on the basis of the  
 60 present experiments because the ion production is  
 61 influenced by many factors, such as the order of elution. In  
 62 any case, it is evident that PAHs having IP lower than or  
 63 equal to 7.45 eV were detected by APLI. In contrast, PAHs  
 64 having IP higher than or equal to 7.48 eV were not detected  
 65 by APLI under our experimental conditions. Based on this  
 66 fact, we can conclude that a nonresonant three-photon (6.99  
 67 eV) rather than a nonresonant four-photon (9.32 eV)  
 68 ionization process is more likely to be operative in the cases  
 69 of anthracene and other PAHs. Consequently, the actual  
 70 ionization potentials of the detected PAHs were lower than  
 71 or equal to 6.99 eV. The maximum ionization potential  
 72 lowering was estimated to be 0.46 eV.

73 Benzo[k]fluoranthene, whose IP (7.48 eV) is slightly  
 74 higher than the above-mentioned IP threshold, was not  
 75 detected by APLI but was detected by APCI. It should be  
 76 mentioned that the PAHs detected by APLI have PAs higher  
 77 than 8.98 eV, while the PA of benzo[k]fluoranthene is 8.87  
 78 eV. Therefore, we conclude that there are additional  
 79 thresholds for APLI detection under our experimental  
 80 conditions. The first is the IP of PAHs, which determines  
 81 whether the primary ion  $M^{+}$  is formed. The second  
 82 threshold is the PA of PAHs, which regulates the hydrogen  
 83 abstraction of  $M^{+}$  to form the secondary ion  $MH^{+}$ . As the  
 84 efficiency of hydrogen abstraction is determined by both IP  
 85 and PA,<sup>14</sup> the threshold of APLI may be more severe than  
 86 that of APCI.

87 We reveal that the fragmentation- and background-free  
 88 detections by APLI<sup>8,16</sup> are also possible with a sub-  
 89 nanosecond visible laser. Ionization of an eluent requiring at  
 90 least five (MeOH) or six (MeCN) 532 nm photons is almost  
 91 impossible, because the order of the absorption cross section  
 92 decreases by about  $10^{33}$  as the order of the multiphoton  
 93 process increases.<sup>21</sup> We suggest that the success of APLI  
 94 with a visible laser extends the possibility of APLI, since  
 95 only several ionization wavelengths in the UV region have  
 96 been examined by APLI thus far. Because there is a degree  
 97 of freedom to choose the optimal excitation and  
 98 fluorescence wavelengths in the case of a fluorescence  
 99 detector coupled with LC, our results show that APLI with a  
 100 wavelength-tunable visible laser will provide an approach  
 101 that is sensitive to ionization potential, i.e., a solvation-  
 102 sensitive ionization method.

103 Nonresonant multiphoton ionization processes have  
 104 been extensively used in studies for isolated molecules in  
 105 gas phase. During the history of nonresonant multiphoton

1 ionization studies, the ionization potentials measured in a  
 2 vacuum have been referred to discuss the ionization  
 3 behavior. The present work shows a possible method for  
 4 investigating the actual threshold of the ionization potential  
 5 of solvated molecules, since the degree of solvation can be  
 6 controlled by changing the condition of LC-MS. More  
 7 accurate determination of the ionization potential of  
 8 solvated molecules is possible by tuning the ionization  
 9 wavelength in the visible region. Because a more powerful,  
 10 wavelength-tunable and short-duration picosecond laser is  
 11 expected to appear in the near future,<sup>22</sup> we can expand the  
 12 applicable substances and eluents.

13  
 14 The present research was partially supported by JST  
 15 PRESTO program and JSPS KAKENHI Grant Numbers  
 16 JP23550102 and JP26107002 in Scientific Research on  
 17 Innovative Areas "Photosynergetics."

18  
 19 Supporting Information is available on  
 20 [http://dx.doi.org/10.1246/cl.\\*\\*\\*\\*\\*](http://dx.doi.org/10.1246/cl.*****).

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## 22 References and Notes

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## Graphical Abstract

## Textual Information

A brief abstract	Atmospheric pressure laser ionization using a compact sub-nanosecond visible laser attached without modification to a conventional liquid chromatograph-mass spectrometer is utilized to detect polycyclic aromatic hydrocarbons. The nonresonant multiphoton process achieved by a visible laser is useful to investigate the ionization potential of solvated analytes compared with the use of the resonant enhanced two-photon process by using an ultraviolet laser.
Title	Eluent-assisted Nonresonant Multiphoton Ionization of Polycyclic Aromatic Hydrocarbons in a Liquid Chromatograph-Mass Spectrometer
Authors' Names	Naoki Oya and Tomoyuki Yatsuhashi

## Graphical Information

