

# Investigation of trace *p*-dichlorobenzene using laser mass spectrometry

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The time-of-flight mass spectrum (TOFMS) relative to the resonant two-photon ionization of gas phase *p*-dichlorobenzene was obtained in the wavelength range of 240 – 250 nm by a home-made system. A special design was made to reduce the effect of memory on the inner wall of the sample inlet system suitable for the investigation of semi-volatile organic compound. In this wavelength range, *p*-dichlorobenzene molecules firstly absorbed one photon to be excited from the ground state  $^1A_g(S_0)$  to the first excited state  $^1B_{2u}(S_1)$ , then absorbed another photon to be ionized. The relationship between the signal intensity of *p*-dichlorobenzene molecular ion  $C_6H_4^{35}Cl_2^+$  at 248-nm wavelength and the laser power was given. The 1.52 power index of  $C_6H_4^{35}Cl_2^+$  was a typical identification of the 3/2 power law. The relationship between the ion signal intensity of  $C_6H_4^{35}Cl_2^+$  and the sample concentration was close to a linear one in the ppm(V/V) range, which led to a detection limit of 125 ppb(V/V) for *p*-dichlorobenzene.

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Organic compounds and especially chlorinated aromatic compounds are important environmental pollutants, which are the most common toxic hazardous air pollutants (HAPs). Study shows that many pollutants are produced by the combustion processes taking place in motorized vehicles or industrial incinerators, one of which is *p*-dichlorobenzene. *p*-dichlorobenzene is widely used as an insect killer and space deodorizer. The presence of *p*-dichlorobenzene in the environment can be hazardous to humans. Exposure can damage the lungs, liver, kidneys, and blood cells. It is also likely to cause human carcinogen based on sufficient evidence of a carcinogenicity in experimental animals. Environmental protection agency (EPA) regulates the levels of *p*-dichlorobenzene in drinking water. The highest level of *p*-dichlorobenzene allowed in drinking water is 0.075 ppm. The Occupational Safety and Health Administration has set a limit for *p*-dichlorobenzene of 75 ppm in the workplace. Nowadays many studies show that *p*-dichlorobenzene can also be used as a surrogate for monitoring numerous other toxic chlorinated hydrocarbons such as dioxins from incinerators<sup>[1,2]</sup>. From the viewpoint of environmental protection and human health, several variations of monitoring technique for trace compound were studied. Laser-based methods have a potential to be better suited for real time analysis<sup>[3–8]</sup>. Especially, laser photoionization with simple time-of-flight mass spectrum (TOFMS) is thought to be one of the most powerful methods for chemical analysis and on-line trace detection. U. Boesl *et al.* developed a new mobile laser mass spectrometer and applied it to on-line measurements at a waste incineration pilot plant, achieving the detection limit for naphthalene in the 10 ppt(V/V) concentration range<sup>[3]</sup>. The detection limit for chlorobenzene on the order of tenth ppb(V/V) was obtained by using vacuum ultraviolet single-photon ionization TOFMS<sup>[4]</sup>. The (2 + 1) resonance-enhanced multiphoton ionization/TOFMS of trichloroethylene and tetrachloroethylene were studied

in the range of 305.0 – 325.0 nm. The detection limits of chloroethylenes at  $\mu\text{g/L}$  concentration range were presented<sup>[5]</sup>. To reduce the condensation effects at room temperature, a special heatable sample inlet system with an effusive nozzle was constructed in our lab to import a semi-volatile compound into the ionization region of TOFMS. Different concentrations of a sample gas were prepared and analyzed. The relationship between the signal intensity of molecular ion  $C_6H_4^{35}Cl_2^+$  ( $m/e=146$ ) and the sample concentration was close to a linear one in the ppm(V/V) range, which led to a limit of detection of 125 ppb(V/V) for *p*-dichlorobenzene in our present experimental conditions.

The scheme of resonant two-photon ionization process of *p*-dichlorobenzene at 248-nm wavelength is illustrated in Fig. 1. The photon energy corresponding to wavelength of 248 nm is about 5.0 eV. The *p*-dichlorobenzene molecules firstly absorb one photon to be excited from the ground state  $^1A_g(S_0)$  to the first excited state  $^1B_{2u}(S_1)$ , then absorb another photon to be ionized. The excitation is subject to more or less sharp resonance conditions depending on the structure of its gas phase ultraviolet (UV) spectrum. Only when the resonance

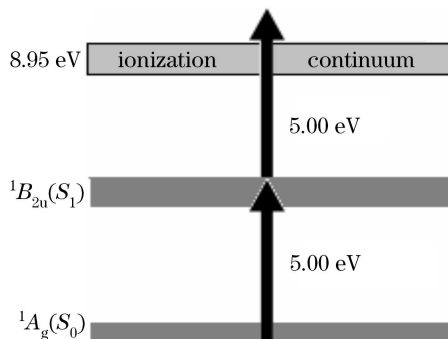


Fig. 1. Resonant two-photon ionization process of *p*-dichlorobenzene at 248-nm wavelength.

conditions for the first absorption step are fulfilled and selective excitation takes place, the second photon can be absorbed up to the ionization continuum with adequate efficiency. Resonance-enhanced and therefore species-selective multiphoton ionization, applied to a mixture of gases located in the electric field between two electrodes, results in a species-selective ion source. Laser mass spectrometry is a fast two-dimensional (2D) analytical technique that combines gas phase UV spectroscopy and TOFMS. It is a promising way to fulfill the requirements of rapid response time, high selectivity and sensitivity, and to realize the detection of target compounds from a complex mixture.

A heatable sample inlet system was designed to import a semi-volatile organic compound of certain concentration into the ionization region of TOFMS. The schematic diagram of the sample inlet system for the experiment setup is illustrated in Fig. 2. The sample inlet system is heated by heating tape. Mixture of trace *p*-dichlorobenzene in air at near one atmospheric pressure is fed into a stainless steel vacuum chamber through a U type tube. The ionization region of the TOFMS is of the classic dual field type described by Wiley and McLaren<sup>[9]</sup>. The voltages of +200 V, -200 V, and -2400 V were maintained on the left, middle, and right acceleration plates respectively. The axis of the molecular beam is passed midway between the two left plates. The REPMI laser is focused on the intersection of the vertical molecular beam axis. The laser is a tunable dye laser (Quantel, TDL90) employing DCM dye, pumped by a Nd:YAG laser (Quantel, Brilliant B, 532 nm). The output is frequency doubled and mixed with the fundamental beam of Nd:YAG to produce a tunable wavelength output from 240 to 250 nm. The laser beam is focused by a quartz lens ( $f = 27$  cm) to interact with the sample gas in the ionization region of TOFMS. The energy of each laser pulse is 10 – 100  $\mu$ J with a pulse duration less than 10 ns. The ions are received at the end of 1.1-m flight tube by a dual Micro-channel Plates (MCP). The ion signal is amplified and recorded by a transient recorder card (F9800) plugged into a personal computer for data acquisition and processing.

In Fig. 3, the TOFMS of *p*-dichlorobenzene at 248-nm wavelength is shown. It is obvious that there are two kinds of ions: the parent ions including  $C_6H_4^{35}Cl_2^+$  ( $m/e=146$ ),  $C_6H_4^{35}Cl^{37}Cl^+$  ( $m/e=148$ ) and  $C_6H_4^{37}Cl_2^+$  ( $m/e=150$ ), and the fragment ions including  $C_6H_4^{35}Cl^+$  ( $m/e=111$ ),  $C_6H_4^{37}Cl^+$  ( $m/e=113$ ) and  $C_6H_5^+$  ( $m/e=77$ ). These three fragment

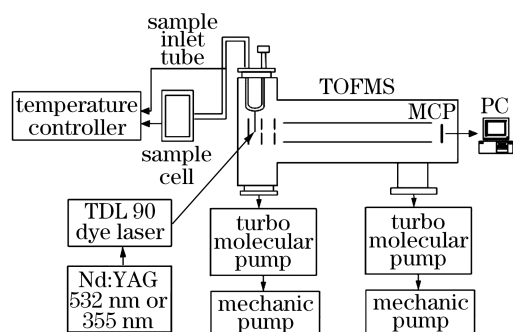


Fig. 2. Scheme of experimental setup.

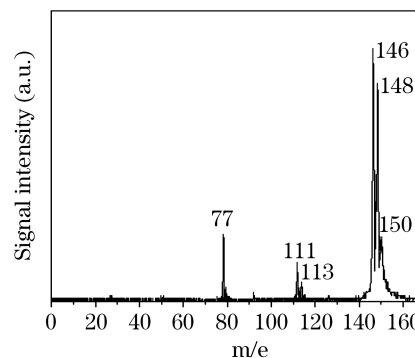


Fig. 3. TOFMS of *p*-dichlorobenzene at 248-nm wavelength.

species are probably produced from the dissociation of the molecular ions. The relative natural abundances due to the chlorine isotopes for *p*-dichlorobenzene is about 9.3:6.1:1 for the masses 146:148:150. But the parent ion intensities observed in Fig. 3 will vary depending on the laser wavelength because the transition band exhibits a small isotope shift<sup>[10,11]</sup>.

The ionization potential of *p*-dichlorobenzene is 8.95 eV ( $72101$   $cm^{-1}$ ). Considering the photon energy of the laser used in our experiment, the *p*-dichlorobenzene molecules need to absorb at least two photons to be ionized, one photon for resonant excitation and the other photon for ionization<sup>[12–14]</sup>. The REMPI mass spectra of *p*-dichlorobenzene at three different excitation wavelengths with a constant laser energy intensity are shown in Fig. 4. It is obvious that the *p*-dichlorobenzene can obtain a high ionization efficiency at 248-nm wavelength. We choose this wavelength for the trace detection study of *p*-dichlorobenzene. A simple robust excimer laser with output wavelength of 248 nm is a more suitable light source for on-line detection of complex organic compounds.

As is well known, the signal intensity depends upon the sample concentration and the laser intensity. Before investigating the detection limit of *p*-dichlorobenzene, we study the relationship between the signal intensity of *p*-dichlorobenzene and the laser energy. The relationship between the laser energy and the signal intensity of

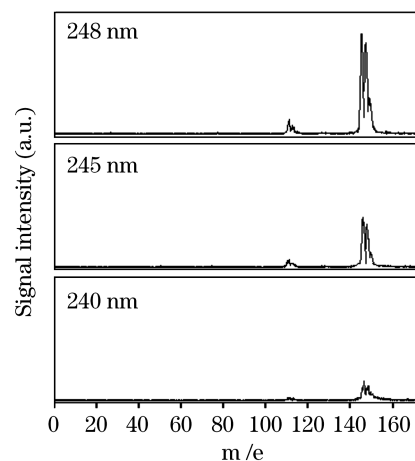


Fig. 4. TOFMS obtained from the ionization of *p*-dichlorobenzene at wavelength of 248, 245, and 240 nm, respectively.

$C_6H_4^{35}Cl_2^+$  at 248-nm wavelength is shown in Fig. 5. It is obtained at the same sample concentration. Linearity of the data is 0.991. The relationship can be expressed as  $\ln S = n \ln I$ , where  $S$  is the signal intensity,  $I$  is the laser energy, and  $n$  is the commonly used "power index" which indicates the photon number absorbed by the molecules from the initial state to the ionization continuum. The power index of  $C_6H_4^{35}Cl_2^+$  we got from the experiment is about 1.5 which is a typical example of the 3/2 power law originating from the geometric effects of the focused laser in the interaction region<sup>[15]</sup>. Power index 1.52 would be used to normalize the ion signal intensity obtained at different laser energies.

The signal intensity of the molecular ion ( $C_6H_4^{35}Cl_2^+$ ,  $m/e=146$ ) at different sample concentrations for the same laser intensity of wavelength of 248 nm is presented in Fig. 6. The *p*-dichlorobenzene sample gases at six different concentrations are prepared in the ppm(V/V) range. The relationship between the ion signal of  $C_6H_4^{35}Cl_2^+$  ( $M = 146$ ) and the sample concentration is close to a linear one in the ppm(V/V) range.

According to the method of Williams, from a TOFMS of the naphthalene permeation standard<sup>[16]</sup>, we are able to achieve the detection limit of *p*-dichlorobenzene in our experimental condition. The detection limit  $d$  is calculated according to the formula  $d = \frac{c}{p-\bar{m}}2\sigma$ . In this formula the variance  $\sigma$  is the noise level between the mass peaks,  $\bar{m}$  is the mean value of the noise as a baseline. The variance  $p$  is the signal peak height of the target molecular in the mass spectrum and  $c$  is the concentration of *p*-dichlorobenzene. The mass spectrum obtained at 248-nm wavelength is shown in Fig. 7, where the concentration is 2 ppm(V/V). The detection limit

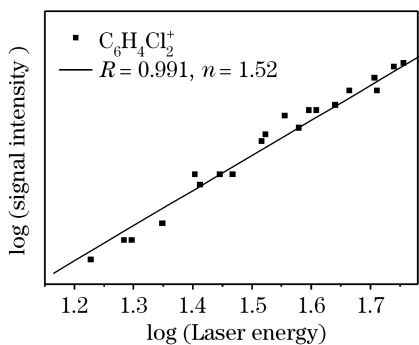


Fig. 5. Relationship between the laser energy and the signal intensity of  $C_6H_4^{35}Cl_2^+$  at 248-nm wavelength.

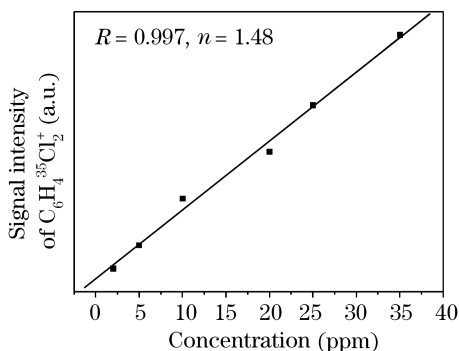


Fig. 6. Relationship between the *p*-dichlorobenzene concentration and the signal intensity of  $C_6H_4^{35}Cl_2^+$ .

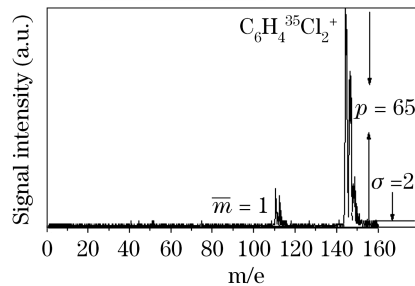


Fig. 7. TOFMS of *p*-dichlorobenzene at 248-nm wavelength (the concentration is 2 ppm(V/V)).

of *p*-dichlorobenzene at 248-nm wavelength is about 125 ppb(V/V).

In summary, a special heatable sample inlet system with an effusive nozzle was made to reduce the memory effect on the inner wall for investigation of semi-volatile organic compound. The (1+1) resonance-enhanced multiphoton ionization/TOFMS of *p*-dichlorobenzene were firstly obtained in the wavelength range of 240 – 250 nm. The characteristics of multiphoton ionization of *p*-dichlorobenzene are analyzed. In this wavelength range, *p*-dichlorobenzene molecules firstly absorb one photon to be excited from the ground state  $^1A_g(S_0)$  to the first excited state  $^1B_{2u}(S_1)$ , then absorb another photon to be ionized.  $C_6H_4Cl_2^+$ ,  $C_6H_4Cl^+$ , and  $C_6H_6^+$  are the major ions generated through the multiphoton ionization processes. The relationship between the signal intensity of *p*-dichlorobenzene molecular ion  $C_6H_4^{35}Cl_2^+$  and the laser power is given. The 1.52 power index of  $C_6H_4^{35}Cl_2^+$  is a typical identification of the 3/2 power law. The relationship between the signal intensity of  $C_6H_4^{35}Cl_2^+$  and the sample concentration is presented. The power index of  $C_6H_4^{35}Cl_2^+$  is 1.52. The detection limit for *p*-dichlorobenzene in ppb(V/V) concentration range at 248-nm wavelength is given in our present experimental conditions.

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