

Rapid detection of trace chloroethylenes using laser mass spectrometry

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Laser mass spectrometry is a new chemical trace analysis method with high selectivity, sensitivity and speed. The mass-resolved resonance-enhanced multiphoton ionization (REMPI) spectra of chloroethylenes—trichloroethylene and tetrachloroethylene are firstly reported in the range 305.0–325.0 nm. The mass-resolved excited spectra and laser power index of fragment ions CCl^+ are presented. The experimental results indicate that 310.8 nm is the suitable ionization wavelength for detection of trichloroethylene and 322.5 nm for the detection of tetrachloroethylene in this wavelength range. The detection limits of these two chloroethylenes of concentration range expressed in $\mu\text{g/L}$ are presented.

Keywords: laser mass spectrometry, resonance-enhanced multiphoton ionization, time of flight mass spectrum, chloroethylenes.

1. Introduction

Trichloroethylene and tetrachloroethylene are important environmental pollutants. The major uses of these two chloroethylenes are as dry cleaning fluids, with some use in the manufacturing of ink, adhesives and paint removers. The presence of these chemicals in environment can be hazardous to humans. Many studies show that the chloroethylenes have relatively high thermal stability that may be useful surrogates for monitoring numerous other toxic chlorinated hydrocarbons emissions such as dioxins from municipal and hazardous waste incinerators [1, 2]. Therefore, there is a growing need for rapid ultrasensitive detection of these persistent organic pollutants (POPs). Laser mass spectrometry is a fast two-dimensional analytical technique which is one of the promising methods for trace pollutants analysis and has been proposed for the continuous monitoring of stack gas emissions from hazardous waste incinerators. The achievement of optimum selectivity with the laser mass spectrometry technique requires detailed characterization of the REMPI spectral signatures of species of interest. Spectroscopic studies of chloroethylenes have been reported by many groups. The vacuum-ultraviolet (VUV) absorption spectra of the chloroethylenes were studied firstly by MAHNCKE and NOYESS [3] in 1935. BERRY [4] recorded VUV spectra, up to 70000 cm^{-1} , for all the chloroethylenes, although an analysis was not

presented. High-resolution photoelectron spectroscopy was performed on the chloroethylenes by LAKE and THOMPSON [5]. Kupperman and co-workers reported electron impact studies of the chloroethylenes [6]. Studies of the excited electronic states of the chloroethylenes were comprehensively reviewed in the monographs of ROBIN [7, 8]. WILLIAMS and COOL [9] investigated the resonance ionization spectroscopy of the chloroethylenes.

Although many investigations have been performed on the chloroethylenes, more studies are needed to realize the trace detection of these species. The purpose of this study is to identify the spectral features most suitable for laser mass spectrometry detection. In the present work, mass-resolved REMPI spectra of trichloroethylene and tetrachloroethylene in the range 305.0–325.0 nm are recorded. The detection limits of chloroethylenes for concentration range expressed in $\mu\text{g/L}$ are presented.

2. Principles of laser mass spectrometry

Development and application of new technologies for on-line monitoring of trace components are current trend in industrial and environmental analytical processes [10–15]. Laser mass spectrometry is a fast two-dimensional analytical technique which is the combination of two different analytical approaches: UV spectroscopy and time-of-flight mass spectroscopy. The first dimension is realized by the REMPI processes and the second is provided by the mass discrimination.

The characteristic process of $m + n$ REMPI is that molecules firstly absorb m -photon energy to their intermediate excited states, and then the excited molecules further absorb other n -photon energy and get ionized. On the left-hand side of Fig. 1, a one-color, two-photon REMPI excitation/ionization scheme is shown. This scheme can be used when the first electronic excited state S_1 lies more than half way to the ionization continuum. On the right-hand side of Fig. 1, a two-color two-photon REMPI excitation/ionization scheme is shown. This scheme can be used when the first electronic excited state S_1 lies less than half way to the ionization continuum.

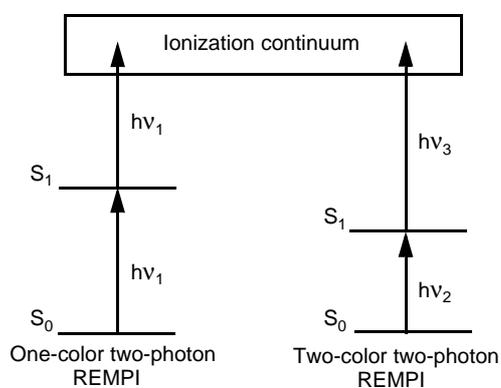


Fig. 1. Diagram of the REMPI process.

The ideal light sources are tunable pulsed laser which can excite different molecular species at their strongest absorption peak and thus reach the best detection limits. The time of flight mass spectrometer (TOFMS) has many advantages which lie in the simplicity, high speed and sensitivity, and has been a popular choice for on-line analysis. For each laser pulse an entire mass spectrum can be obtained. A perfect combination of these techniques has become the most promising analysis tool in industrial and environmental processes.

3. Experimental setup

The pulsed supersonic molecular beam/REMPI/time-of-flight mass spectrometer engaged in our work is illustrated in Fig. 2. A mixture of trace trichloroethylene or tetrachloroethylene in helium carrier gas near atmospheric pressure was fed into stainless steel vacuum chamber through the pulsed valve (Parker Company, USA) at 10 Hz repetition. The ionization region of the TOFMS was of the classic dual field type described by Wiley and McLaren. The voltages of +100 V, -100 V and -2400 V were maintained on the left, middle, and right acceleration plates, respectively. The axis of the molecular beam passed midway between the left two plates. The laser beam was focused at the intersection of the vertical molecular beam axis. Ionization light used in the experiment was produced by a tunable dye laser (TDL90, Quantel), which was pumped by the second harmonic of Nd:YAG (Brilliant B, Quantel). A digital/delay pulse generator (SRS, DG535) was used to trigger the pulsed valve and the laser with appropriate delayed time at fixed repetition rate (10 Hz). The fundamental output of the dye laser (DCM) was frequency doubled and produced tunable wavelength ranging from 305.0 to 325.0 nm. The energy of each laser pulse was several millijoules with pulse duration around 6 ns.

The ions were received at the end of 1.1 m long flight tube by dual multi-channel plates (MCP). The ion current signal was amplified and recorded through a transient

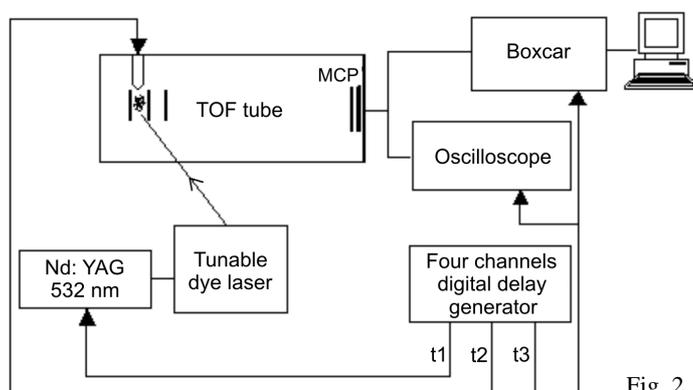


Fig. 2. Scheme of REMPI-TOFMS setup.

recorder card (EGG 9846) plugged in a personal computer which recorded the mass spectrum. In the experiment, each mass spectrum was averaged over 100 shots to increase signal to noise ratio (S/N). For REMPI laser wavelength scans, the signal of a given mass channel was monitored with boxcar signal averager (Stanford Research Systems, SR250 and SR245), the output of which was digitized and stored by the computer.

4. Results and discussion

Figure 3 displays the REMPI photofragment mass spectra of C_2HCl_3 and C_2Cl_4 , respectively. Figure 3a is the mass spectrum of C_2HCl_3 when exposed to a dye laser beam of 5 mJ and a wavelength of 310.8 nm corresponding to the origin of the $3d \leftarrow \pi$ two-photon transition. Figure 3b is the mass spectrum of C_2Cl_4 when exposed to a dye laser beam of 6 mJ and wavelength of 322.5 nm corresponding to the band of the $3p \leftarrow \pi$ two-photon transition. The CH^+ and C_2H^+ ion fragments are shown in Fig. 3a and these cannot be found in Fig. 3b. The parent ions of these two species have not been found in our experimental wavelength range. The prominent peaks corresponding to Cl^+ and CCl^+ ion fragments are shown in the two mass spectra. The result can be explained by the fact that the laser intensities are high enough so that simple three photon ionization of the parent molecule is only the first step in a more complicated sequence of single photon absorptions by the parent ion and smaller ion fragments. The parent ion formed by three photon ionization, resonant at the two photon level then absorbs an additional photon followed by rapid internal conversion [16]. Fragmentation of the vibrationally excited parent ion greatly exceeds the rate for absorption of an additional photon. The Cl^+ and CCl^+ ion fragments are formed by the

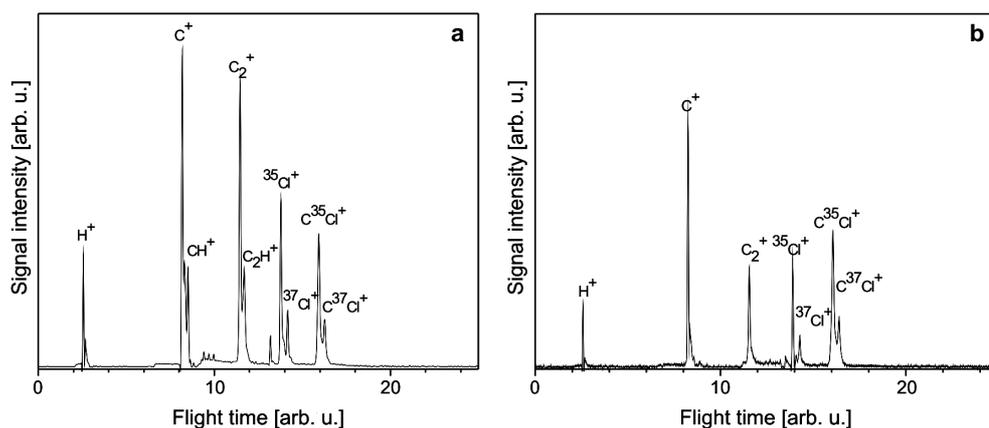


Fig. 3. REMPI photofragment mass spectrum for C_2HCl_3 following two-photon resonant excitation of the $3d \leftarrow \pi$ transition at 310.8 nm (a), and REMPI photofragment mass spectrum for C_2Cl_4 following two-photon resonant excitation of the $3p \leftarrow \pi$ transition at 322.5 nm (b)

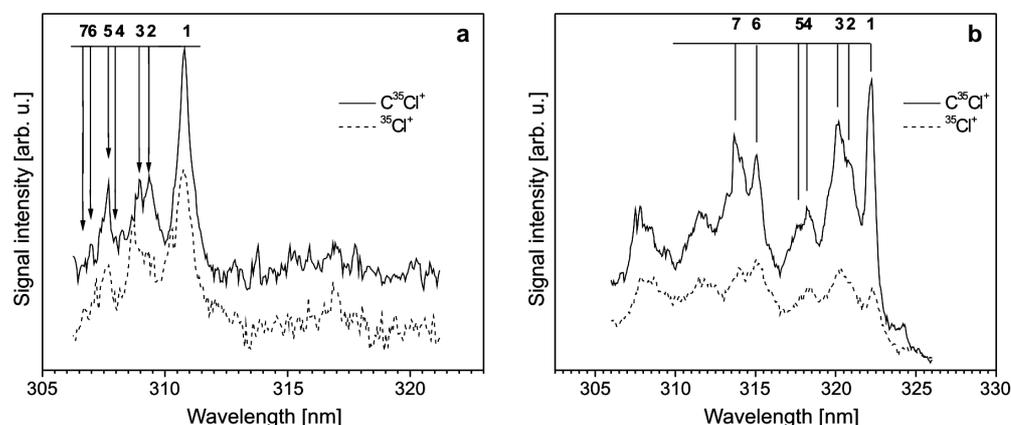


Fig. 4. Two-photon vibronic spectrum of the $3d \leftarrow \pi$ transition of C_2HCl_3 (a) and two-photon vibronic spectrum of the $3p \leftarrow \pi$ transition of C_2Cl_4 (b) in the range 305.0–325.0 nm.

absorption of many photons, and the CCl^+ ion fragments are found to be useful for REMPI detection of trichloroethylene and tetrachloroethylene.

The ionization potential of C_2HCl_3 is 9.48 eV (about 76490 cm^{-1}), and the ionization potential of C_2Cl_4 is 9.33 eV (about 75216 cm^{-1}). In 305.0–325.0 nm wavelength range, these two sample molecules firstly absorb two-photon energy to their Rydberg state, then the excited molecules further absorb additional photon energy and get ionized. A decoupled series of one-photon absorptions, internal conversions, and fragmentation may then occur along absorption ladders of this ion fragment and several other possible sequentially formed Cl^+ and CCl^+ ion fragments. Figure 4

T a b l e. The $3d \leftarrow \pi$ bands of C_2HCl_3 and $3p \leftarrow \pi$ bands of C_2Cl_4 .

Sign	C_2HCl_3 : $3d \leftarrow \pi$ bands		C_2Cl_4 : $3p \leftarrow \pi$ bands	
	Two-photon energy [cm^{-1}]	Assignment	Two-photon energy [cm^{-1}]	Assignment
1	64350	0_0^0	62015	$B_{\beta_g} 1_0^2$
2	64642	8_0^1	62346	$B_{\alpha_g} 1_0^3$
3	64750	7_0^1	63493	$B_{\beta_g} 1_0^2 2_0^1$
4	64935	8_0^2	62839	$B_{\alpha_g} 1_0^3 2_0^1$
5	65003	6_0^1	63455	$B_{\beta_g} 1_0^3$
6	65149	7_0^2	63681	$B_{\alpha_g} 1_0^4$
7	65221	8_0^3	63715	$A_g 1_0^4$

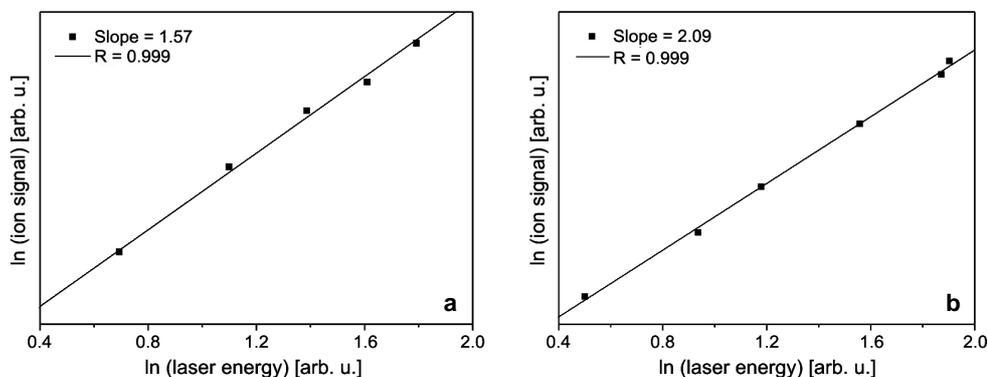


Fig. 5. Relationship between laser energy and signal intensity of CCl⁺ ion fragment produced by C₂HCl₃ at 310.8 nm (a), and the relationship between laser energy and signal intensity of CCl⁺ ion fragment produced by C₂Cl₄ (b).

displays two-photon vibronic spectrum of the $3d \leftarrow \pi$ transition of C₂HCl₃ and two-photon vibronic spectrum of the $3p \leftarrow \pi$ transition of C₂Cl₄ in the range 305.0–325.0 nm. The two-photon REMPI spectra of C₂HCl₃ and C₂Cl₄ are the Rydberg excitations of a π electron from C=C double bond. The tentative assignments of some of the prominent vibronic bands for each of the Rydberg transitions of C₂HCl₃ and C₂Cl₄ are given in the Table. From the assignment, three vibrational frequencies ($3d \leftarrow \pi$) of C₂HCl₃ can be calculated: $\nu_6 = 653 \text{ cm}^{-1}$, $\nu_7 = 400 \text{ cm}^{-1}$ and $\nu_8 = 291 \text{ cm}^{-1}$. Two vibrational frequencies ($3p \leftarrow \pi$) of C₂Cl₄ can be calculated: $\nu_1 = 1390 \text{ cm}^{-1}$ and $\nu_2 = 486 \text{ cm}^{-1}$.

The most suitable wavelength for trace detection of C₂HCl₃ and C₂Cl₄ in our wavelength range can be determined from Fig. 4. It is obvious that for C₂HCl₃, the signal intensity of CCl⁺ ion fragment is very strong at 310.8 nm, and for C₂Cl₄ the signal intensity of CCl⁺ ion fragment is very strong at 322.5 nm. This indicates that the C₂HCl₃ and C₂Cl₄ sample molecules get high ionization efficiency at these

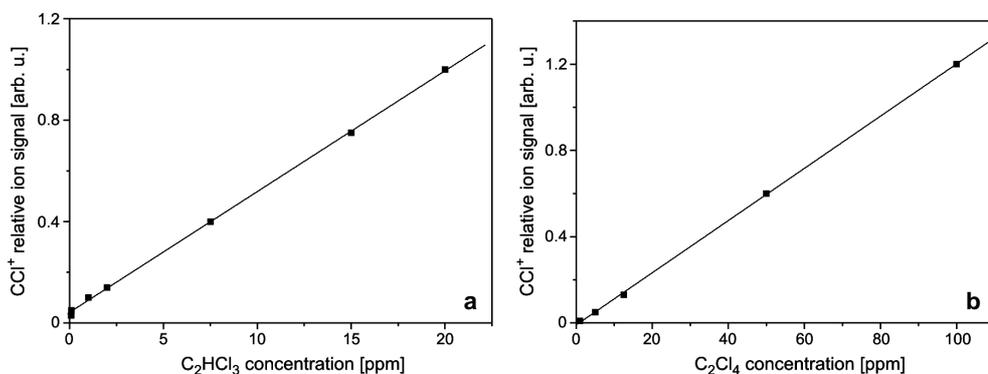


Fig. 6. Linear variation with C₂HCl₃ concentration of the CCl⁺ ion fragment REMPI signal at 310.8 nm (a), and linear variation with C₂Cl₄ concentration of CCl⁺ ion fragment REMPI signal at 322.5 nm (b).

two wavelengths, respectively. It is known that there is a linear relation between signal S and sample concentration n , and the ionization efficiency is also relative to laser intensities I . The formula can be illustrated as $S = cnI$, where c is a coefficient that is different for different molecular species [17, 18]. The relationship between laser intensity and signal intensity of CCl^+ ion fragment is displayed in Fig. 5.

In our experiment the laser intensities and signal intensity of CCl^+ ion fragment are recorded at every sample concentration. According to the relationship between laser intensity and signal intensity of CCl^+ ion fragment, we get the detection limits of the two species. Detection limit is defined as the sample concentration in helium gas at about 1 atm pressure. Figure 6 shows the linear relation between sample concentration of the two chloroethylenes and signal intensity of CCl^+ ion fragment. At 310.8 nm, the detection limit of C_2HCl_3 is 0.2 $\mu\text{g/L}$ ($S/N = 2$), and at 322.5 nm, the detection limit of C_2Cl_4 is 6.0 $\mu\text{g/L}$ ($S/N = 2$). The unknown concentration of C_2HCl_3 and C_2Cl_4 sample gas can be determined at $\mu\text{g/L}$ concentration level using laser mass spectrometry technique according to our experiment data.

5. Conclusions

Laser mass spectrometry is a new chemical trace analysis method with high selectivity, sensitivity and speed. The mass-resolved REMPI spectra of trichloroethylene and tetrachloroethylene are firstly obtained in the range 305.0–325.0 nm. The study shows that 310.8 nm is the suitable wavelength for detection of trichloroethylene and 322.5 nm is the suitable wavelength for detection of tetrachloroethylene in this wavelength range. The detection limits of these two chloroethylenes for concentration range expressed in $\mu\text{g/L}$ are presented.

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