Journal of Photochemistry and Photobiology A: Chemistry 220 (2011) 31–38

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Multiphoton dissociation and vibrational mediated dissociation of chlorinated methanes, $CH_{4-n}Cl_n$ ($n = 2, 3, 4$) at 355 nm

J.C. Poveda*, A. Guerrero, I. Álvarez, C. Cisneros

Laboratorio de Colisiones Atómicas Moleculares y Óptica, Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, Cuernavaca, Morelos, México C.P. 62210

ARTICLE INFO

Article history:
Received 10 December 2010
Received in revised form 15 February 2011
Accepted 14 March 2011
Available online 21 March 2011

Keywords:
Chlorinated methanes
Photoionization
Photodissociation
Dissociation pathways
Vibrational mediated photodissociation

ABSTRACT

In this paper, the experimental results for the photodissociation, PD, and photoionization, PI, of chlorinated methanes, CH_2Cl_2, $CHCl_3$, and CCl_4, studied by cooled molecular jets and Time of Fly Mass Spectrometry detection, ToF-MS, are presented. Photodissociation processes outcome from multiphoton absorption at 10^9–10^{10} W cm^{-2} intensities at 355 nm laser radiation. The results indicated that photodissociation dominates over photoionization processes as some detected ions are originated from the absorption of up to five photons. The main dissociative channels lead to the formation of H^+, C^+, CH^+, $CH_2{}^+$, $^{35}Cl^+$, $^{37}Cl^+$, $C^{35}Cl^+$, and $C^{37}Cl^+$. The analysis of the ratio of ion yield from different isotopologues for each molecule, as a function of the energy per pulse, showed that the formation of the more abundant ions: Cl^+ and CCl^+, is strongly influenced by changes in the vibrational structure of the excited states as a consequence of the two different stable chlorine atoms. As a first approach to get some insight of the experimental results, the ground state vibrational energy levels for chlorinated methanes, were calculated using Density Functional Theory. From the abovementioned calculations was possible to think that the changes in energy of the vibrational levels drive the ion yield of observed ions due to different isotopic composition of chlorinated methanes.

1. Introduction

The versatility of industrial use of halogenated hydrocarbons, usually chlorinated and fluorinated, with one and two carbon atoms, especially used as refrigerants, dielectrics, pesticides and anthropogenic emissions, make the further fate of these ions and their secondary products as an important subject of research. Chlorinated hydrocarbons such as CH_2Cl, $CHCl_2$ and CCl_3 radicals are some of the most important secondary products from combustion processes, in particular when hazardous waste is finally incinerated [1]. Also when these compounds are dumped to the atmosphere, they can migrate to higher altitudes, as stratosphere [2], where halomethanes are exposed to ultraviolet, low pressure, and ionization radiations from solar or cosmic origin. At these conditions the halogenated molecules produce a wide variety of halogenated radicals and ions which interact with ozone through different processes that perturb the free radical chemistry within it; being the O_3-radicals interactions the major channels of catalytic ozone deployment [2].

The experimental work about the ionization and dissociation processes of single molecules produced by single and multiple photon absorption, or by strong electric fields are excellent analytical tools to understand the mechanisms responsible of the primary rupture of chemical bonds. The first energy levels of chlorinated methanes and their vibrational structure were measured previously by using vacuum ultraviolet absorption spectroscopy [3], and emission spectroscopy [4]. Also, core photoelectron spectroscopy was used to resolve the vibrational structure of chloromethane series $CH_{4-n}Cl_n$ [5]. The photodissociation of $CHFCl_2$ and $CHCl_3$ was analyzed using 193 nm radiation [6] and the dynamics of H atom ejection in the photodissociation of chloromethanes [7] as a way to explore its photochemical pathways. Dissociative single photon ionization of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 was measured in the 10.0–13.5 eV range [8,9], being CH_2Cl^+, $CHCl^+$, CCl^+ the most important dissociative channels. Vacuum-UV fluorescence spectroscopy of $CHCl_3$ in the range of 8–30 eV used to measure *pre-* and *post*-ionization channels was reported some time ago [10,11]. In the range of intense laser fields, pico- and femto-second pulses, up to 10^{13} W cm^{-2}, dissociation processes dominate over multiphoton ionization process [12]. The later experiments have shown that multiple charged daughter ions, C^{3+}, C^{2+}, Cl^{4+}, Cl^{3+}, CCl^{2+}, are some of the main products of molecule-laser radiation interaction at high laser intensities [12]. Using resonance enhanced multiphoton ionization, the effect of deuterium, isotopic effect, on the vibrational frequencies of $CHCl_2$ was analyzed [13,14]; the interchange hydro-

---

* Corresponding author. Tel.: +52 777 3172588.
E-mail address: jkclimb@fis.unam.mx (J.C. Poveda).

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.03.010

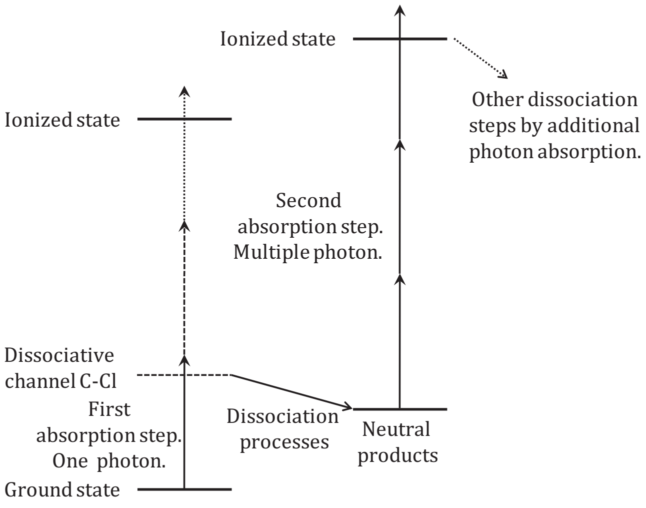

Fig. 1. Photodissociation–photoionization mechanism in chlorinated methanes.

gen per deuterium produces red shift in vibrational structure of $CDCl_2$.

Some of the previous theoretical work include *ab initio* calculations under zero-field conditions which do not take into account the influence of an intense laser electric field on molecular electron density distributions on chlorinated methanes, to evaluate ionization energies, electronic and vibrational levels [7], and C–H and C–X (X = F, Cl, Br) bond dissociation energies, BDEs [15–18]. Two dissociation mechanisms: single neutral and charged atom and two-atom molecules elimination were previously analyzed [19,20]. In the later case, the analysis of the energy barrier for transition structures was taken into account too [18,19]. Theoretical methods include Density Functional Theory, DFT [18,19], CBS-Q methods [16], Möller–Pleset theory, MP_2 and MP_4 [9], and QCSID (T) [9].

In the present work, the photoionization and photodissociation of chlorinated methanes, $CH_{4-n}Cl_n$ ($n = 2, 3, 4$), at 355 nm were analyzed. Ions produced from molecular dissociation and ionization processes were identified using a linear time of flight mass analyzer, L-ToF-MA. From experimental data, the ion yield profile for the most abundant ions was obtained, and the number of absorbed photons along the energy calculated. The data were compared with previous reports by Sharma [19,20], where the molecular ion signal was nonexistent for both compounds, dichloromethane and trichloromethane, with very similar fragmentation patterns observed when data were compared with our results. Also, *ab initio* molecular electronic structure calculations were performed to aim to understanding the fragmentation pattern of these molecules in the laser field. The energy of different dissociation channels was calculated. On comparing theoretical results with experimentally observed ion signals and their relative abundances in ToF-MS, it is inferred that these molecules undergo sequential Cl atom elimination followed by photoionization of the fragments, Fig. 1 shows a sequential mechanism which help to finding a reasonable explanation of the experimental results. The main goal of our research is to show the effect of the two stable isotopes of chlorine atom on the vibrational structure of chlorinated methanes through the ratios of different products containing either ^{35}Cl or ^{37}Cl. Changes in the vibrational frequencies can mediate the photon absorption through excited electronic states, S_n, a mechanism denominated vibrational mediated dissociation *VMD* [21], which has been observed in different small molecules as water [22,23], CH_3Cl [24], and others. To assess the change of vibrational frequencies, resulting from possible isotopologues of chlorinated methanes, a ground electronic state calculation was performed by vibrational analysis density functional theory using a B3LYP functional and a 6-311G(3df,2p) basis set to construct the wave function (Table 1). The differences in energies, as it can be seen from Table 1, are larger than the spectral width of the laser radiation used here. The experimental evidence of the isotopic effect is analyzed and explained on basis of the two stable isotopes of chlorine, ^{35}Cl and ^{37}Cl, and their vibrational frequencies.

2. Experiment

Experimental setup was described elsewhere [25]. Briefly, vapor from samples, CH_2Cl_2, $CHCl_3$, or CCl_4, was introduced into de ionization chamber through a pulsed valve synchronously coupled with the laser pulses. The ionization chamber was maintained at 10^{-8} Torr provided by two turbo molecular pumps. The opening time of the valve was adjusted to obtain a final pressure of 2×10^{-6} Torr within the chamber. A cooled molecular beam was produced as a consequence of a swift change in pressure, and it was collimated using a skimmer with 0.50 mm aperture located at 10 mm from the inlet. The interaction region was located at 12 cm from the skimmer, between two parallel plates, separated by 6 mm, and continuously polarized at 5.0 and 3.5 kV, acting as extraction and acceleration plates, respectively. In the interaction region the molecular beam cut across perpendicularly with a 355 nm laser radiation from the third harmonic of a Nd:YAG laser (Spectra Physics), with temporal FWHM of 6.5 ns, and 10 Hz repetition rate. Different sets of data were taken when the energy per pulse was progressively changed from 3 to 50 mJ. The laser radiation was focused into the interaction region using a lens of 20 cm focal length reaching intensities of the order of $5 \times 10^{10}\ \mathrm{W\,cm^{-2}}$ at the peak energy per pulse, 50 mJ. The resulting ions traveling orthogonally to the molecular beam and the laser radiation plane into a field free region of 1 meter long were separated accordingly with their mass/charge ratio. Finally, the ions were detected using a channeltron detector, the signal was preamplified and digitized using a multichannel analyzer, EG&G ORTEC. The signal was recorded using 4000 channels with a digital resolution of 5 ns per channel to complete a window of 20 μs. The final ToF spectra are the addition of 5000 laser shots.

3. Results and discussion

Fig. 2 shows the ToF spectra, convoluted to mass/charge ratio, of chlorinated molecules when they are photodissociated at energies per pulse of 10 mJ, the parent ions were not observed. The cooled molecules ejected from the skimmer can absorb more than one 355 nm photon and dissociate very fast as ions or neutral radicals. Neutral fragments can absorb additional photons and further ionized because they can remain a longer time in the interaction region, comparatively with the photon absorption times and the width of laser pulses. The data presented are the result of dissociation–ionization processes, which follow a sequential process as is shown in Fig. 1.

Basically the processes which take place, starting from the neutral molecules follows the sequence:

a. The cool neutral molecules ejected from the skimmer can absorb one or more photons giving neutral fragments, radicals as by-products. The resulting products can reside in the interaction region enough time to absorb more photons.
b. When new absorption processes occur the radicals can be ionized and dissociated and ions are able to be detected.
c. Finally the ions can experience additional dissociation steps to produce lower mass ions by the absorption of additional photons.

Table 1
Calculated[a] vibrational frequencies in the S_0 ground state in cm^{-1}.

	Isotopologues			Identification
	35-35	35-37	37-37	
CH_2Cl_2	281.8	278.4	275.0	CCl_2 scis.
	702.6	699.4	697.0	CCl_2 s-strength
	719.4	717.5	715.0	CCl_2 a-strength
	901.5	901.2	900.9	CH_2 rock
	1173.1	1172.9	1172.7	CH_2 twist
	1286.9	1286.7	1286.5	CH_2 wag
	1465.8	1465.8	1465.8	CH_2 scis
	3114.0	3114.0	3114.0	CH_2 s-strength
	3190.9	3190.9	3190.9	CH_2 a-strength

	Isotopologues				Identification
	35–35-35	35–35-37	35–37-37	37–37-37	
$CHCl_3$	259.9	257.3	255.0	253.1	CCl_3 d-deformation.
	259.9	257.9	255.7	253.1	CCl_3 d-deformation.
	365.0	362.2	359.4	356.4	CCl_3 s-deformation.
	665.9	664.3	662.7	661.3	CCl_3 s-strength
	730.0	728.1	726.6	726.5	CCl_3 d-strength
	732.1	731.8	730.9	728.6	CCl_3 d-strength
	1234.3	1234.1	1234.0	1234.0	CH bending.
	1235.6	1235.5	1235.4	1235.2	CCl_3 d-strength
	3165.7	3165.7	3165.7	3165.7	CH strength

	Isotopologues					Identification
	35–35-35-35	35–35-35-37	35-35–37-37	35–37-37-37	37–37-37-37	
CCl_4	218.2	216.7	215.2	213.7	212.2	CCl_3 deg. deformation.
	218.3	216.8	215.3	213.8	212.3	CCl_3 deg. deformation.
	313.6	309.8	307.8	306.6	305.3	CCl_3 deg. deformation.
	313.7	312.4	309.5	306.7	305.4	CCl_3 deg. deformation.
	313.7	312.6	311.2	309.1	305.5	CCl_3 deg. deformation.
	454.0	451.0	448.0	444.8	441.6	CCl Sym. strength
	741.4	739.9	739.6	739.5	738.9	CCl deg. strength
	741.8	741.7	740.5	739.6	739.4	CCl deg. strength
	742.6	742.3	742.1	741.3	740.2	CCl deg. strength

[a] Calculated at DFT level of theory using a B3LYP hybrid functional and a basis set 6-311G(3df.2p).

It can be a dissociative process where both neutral and charged fragments are present.

The general scheme which can explain this mechanism is:

$$CH_{4-n}Cl_n \quad (n = 2, 3, 4) \xrightarrow{xh\nu} CH_{4-n}Cl_{n-1} + Cl \xrightarrow{yh\nu} CH_{4-n}Cl_{n-1}{}^{\bullet+}$$

$$\rightarrow \begin{cases} CH_{3-n}Cl_{n-1}{}^{+} + H^{\bullet} \\ CH_{4-n}Cl_{n-2}{}^{+} + Cl^{\bullet} \\ CH_{3-n}Cl_{n-2}{}^{\bullet+} + HCl \end{cases}$$

In order to estimate the number of photons absorbed that produce a particular ion, the logarithm of the measured photoion current was plotted as a function of the logarithm of the laser intensity accordingly with [8], the procedure followed is shown in Fig. 3 for the case of tetrachloromethane. The calculated numbers of photons to form the detected ions in the ToF spectra are reported in Table 2. From these data we explain the possible dissociative channels taking place in the formation of the observed ions in the ToF spectra (Fig. 2).

3.1. Dichloromethane

As it was pointed out in the present measurements, the molecular parent ion and heavy ions were not detected. The formation of the resulting ions follows the mechanism previously exposed. The more abundant ions observed were: H^+, $CH_n{}^+$ ($n = 0, 1, 2, 3$), $^{35}Cl^+$, $^{37}Cl^+$, $C^{35}Cl^+$ and $C^{37}Cl^+$; lower quantities correspond to: $H_2{}^+$, $H^{35}Cl^+$, $H^{37}Cl^+$, $CH^{35}Cl^+$, $CH^{37}Cl^+$, $CH_2{}^{35}Cl^+$ and $CH_2{}^{37}Cl^+$. Chiang et al. [9] had observed large amounts of CH_2Cl^+, $CHCl^+$ and CCl^+ with appearance potentials at 12.08, 12.46 and 15.96 eV, respectively, due to post ionization dissociation, in a 11–20 eV region. Using 355 nm radiation and a fixed energy at 10 mJ Sharma had

Table 2
Number of absorbed photons.[a]

Ion	CH_2Cl_2	$CHCl_3$	CCl_4
H^+	4.03	3.10	–
$H_2{}^+$	4.90	–	–
C^+	4.03	3.97	4.03
CH^+	4.08	3.92	–
$CH_2{}^+$	4.07	–	–
$^{35}Cl^+$	4.06	4.04	4.02
$H^{35}Cl^+$	4.06	4.02	–
$^{37}Cl^+$	4.12	4.15	3.99
$H^{37}Cl^+$	d.	3.97	–
$C^{35}Cl^+$	3.03	3.04	3.05
$CH^{35}Cl^+$	3.00	3.08	
$C^{37}Cl^+/CH_2{}^{35}Cl^+$	3.03	3.10	2.98
$CH^{37}Cl^+$	3.15	d.	–
$CH_2{}^{37}Cl^+$	3.09	–	–
$CH^{35}Cl_2{}^+$	–	3.02	–
$CH^{35}Cl^{37}Cl^+$	–	2.99	–
$C^{35}Cl_3{}^+$	–	d.	3.04
$C^{35}Cl_2{}^{37}Cl^+$	–	d.	2.99
$C^{35}Cl^{37}Cl_2{}^+$	–	d.	3.05

[a] For the data analysis and error of about 10% was take in account. d. detected at very low ion currents.

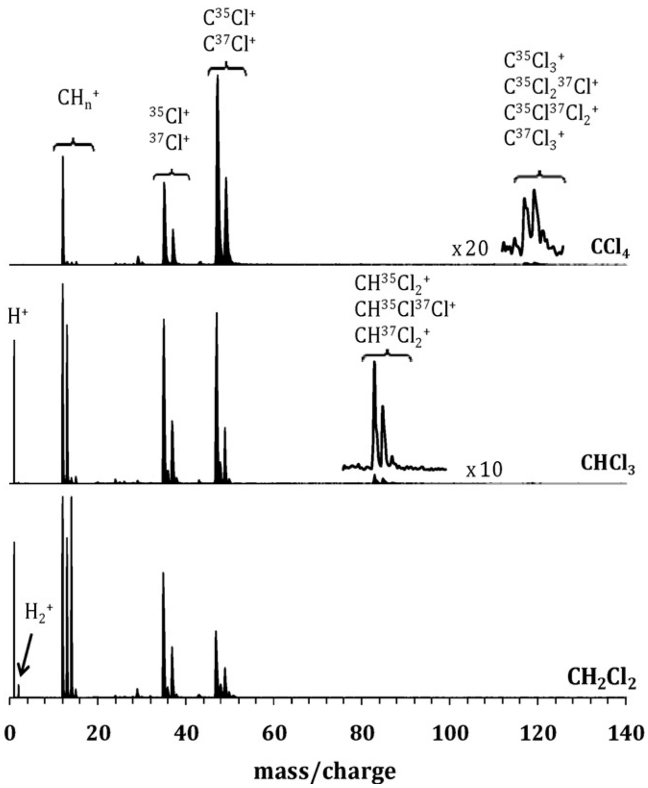

Fig. 2. Convoluted ToF to m/q spectra of chlorinated methanes. PD-PI at 355 nm and 10 mJ per pulse.

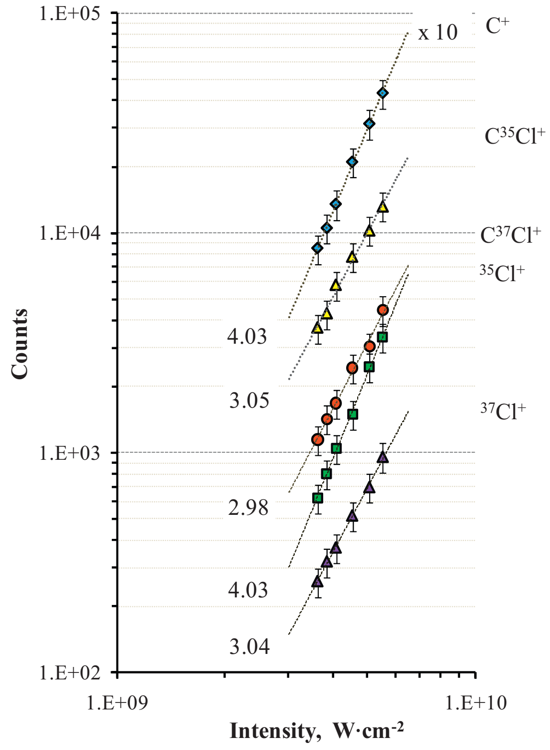

Fig. 3. Ion yields for CCl_4 fragments and calculus of the number of absorbed photons.

reported as the most abundant fragment ions: H^+, $CH_n{}^+$ ($n = 0$, 1, 2), Cl^+, CCl^+, $CHCl^+$ and CH_2Cl^+ [19,20], and lower quantities of $H_2{}^+$ and HCl^+, in good agreement with our results. The main dissociative channels of CH_2Cl_2 molecule producing the detected ions can be represented as:

$$CH_2Cl_2 \xrightarrow{1ph.} \begin{array}{ll} CH_2Cl_2 + Cl & \xrightarrow{3ph.} CH_2Cl^+ \\ CHCl + HCl & \xrightarrow{3ph.} CHCl^+ \\ & \xrightarrow{4ph.} HCl^+ \end{array}$$

In Table 3 we summarize the predissociative channels of the studied molecules. Dichloromethane predissociates by four different ways, channels 1–4. The dissociation energy belonging to each dissociation channel is shown in Table 3. Dissociation channels 1 and 2 are open by the absorption of one 355 nm photon, producing some neutral fragments, this are the lowest energy dissociation channels [9]. And the most probable processes instead of ionization processes requiring 11.315 eV at least. Dissociation processes occurs in a short time of the order of pico seconds, a very short time when it is compared with the temporal laser pulse width. Neutral fragments remain a longer time in the ionization region because they are not subjected to the effect of extraction and acceleration plates. The neutral fragments may absorb additional photons, so it can be ionized in the time within the laser pulse. The formation of the ion CH_2Cl^+, see Table 4, indicates that the two neutral radicals CH_2Cl and Cl can be ionized by the absorption of three and four photons, which have ionization potentials of 8.75 and 12.97 eV, channels 12 and 40 in Table 4, respectively, it is in good agreement with the calculated number of photons from our experimental results reported in Table 2, three and four photos, respectively. Thus, there is a competition between molecular ionization giving $CH_2Cl_2{}^+$, and pre-dissociation to form CH_2Cl and Cl. Neutral radicals are ionized to form CH_2Cl and Cl^+, being $CH_2Cl_2 \rightarrow CH_2Cl \rightarrow CH_2Cl^+$ the most probable low energy dissociation-ionization channel according with Ref. [9].

If the dissociative channel 3 takes place, the formation of $CHCl_2$ is possible but requires the absorption of two photons, with less probability than dissociative channels 1 and 2. The radical $CHCl_2$ has an ionization potential of 8.16 eV [16], see Table 4, which is only 0.59 eV less than that for CH_2Cl, and requires also three photons. The absence of $CHCl_2{}^+$ could be an indication that the H elimination does not occur from the CH_2Cl_2. This can be explained in terms of higher energy for the C–H bond cleavage over the C–Cl bond [19] from Table 3, higher than the energy of one 355 nm photon, and higher than 4.34 eV from the *ab initio* calculations. Also, the formation of CH_2Cl^+ through channel 2 requires a total of 1 + 3 photons, while the formation of $CHCl_2{}^+$ through channel 3, requires 1 + 4 photons. The proposed mechanism involves the dissociation of CH_2Cl_2 into CH_2Cl and Cl, which then can be ionized or dissociated through several distinct competitive channels [19]. The low ion current of CH_2Cl^+ measured reveals that this ion undergoes fast dissociation. Other ions of smaller sizes result directly from the ionization processes. For instance, if the formation of CH_2Cl neutral radical happen, channel 2, it would have a 8.75 eV ionization energy, which is supplied by three photons, which is in good agreement with the calculated number of absorbed photons, reported in Table 2. But also, it can dissociate through different channels to give other neutral fragments, channels 13–15 in Table 4. The detection of HCl^+ is the result of four photons absorption, beginning by the dissociation of CH_2Cl_2 producing HCl and its further ionization. HCl has an ionization potential of 12.72 eV, channel 39 in Table 4, in good agreement with the present results (Table 2).

The formation of lower mass ions, observed in the ToF spectra with the major ion yield, is the result of a fast dissociation of the early analyzed ions. Previous reports [9] propose the formation of CCl^+ near the threshold at 15.96 eV and may proceed via the molecular ionization-dissociation channel $CCl^+ + HCl + H$ rather than $CCl^+ + H_2 + Cl$ channel, but at higher energies the latter dominates [9]. In our experiments the formation of CCl^+ is the result of

Table 3
Pre-ionization dissociative channels of neutral chlorinated methanes.

	Products	Energy, eV	Calculated[a]	Channel	References
CH_2Cl_2	$CHCl + HCl$	3.38	–	1	Ref. [9]
	$CH_2Cl + Cl$	3.46	3.32	2	Refs. [19,32]
	$CHCl_2 + H$	4.22	4.34	3	Ref. [19]
	$CH_2 + 2Cl$	7.54	–	4	Ref. [32]
$CHCl_3$	$CHCl_2 + Cl$	3.10, 3.29	3.01	5	Refs. [20,6]
	$CCl_3 + H$	4.65	4.18	6	Ref. [20]
	$CCl_2 + HCl$	4.67	–	7	Ref. [10]
	$CHCl + Cl_2$	5.63	–	8	Ref. [10]
CCl_4	$CCl_3 + Cl$	2.94, 3.08	2.65	9	Refs. [33–35]
	$CCl_2 + Cl_2$	3.45, 5.57	–	10	Refs. [33]
	$CCl_2 + 2Cl$	5.91, 8.05	–	11	Refs. [33,35]

[a] Calculated using DFT- B3LYP level of theory and basis set 6-311G(3df, 3p).

three photon absorption, of energy up to 10.47 eV, Table 2. Then, the formation of the CCl^+ ion can be interpreted as the result of the fast dissociation of $CHCl^+$ in a vibrational excited state. The mechanism proposed for the formation of $CH_2{}^+$ ion from CH_2Cl^+, which requires the absorption of two additional photons, five in total, is not in agreement with calculated photons, four, see Table 2, corresponding to a sequential mechanism. So, the formation mechanism corresponds to the simultaneous ionization-dissociation, and the calculated number of photons is in agreement with the $CH_2{}^+$ energy as follows

$$CH_2Cl \xrightarrow{4ph.} CH_2{}^+ + Cl$$

The formation of CH^+ ion can be the result from two different dissociative processes, from $CHCl^+$ or CH_2Cl^+, which requires the absorption of additional photons. In a first case the ion eliminates a neutral Cl, channel 33 in Table 4; and in the second case, the dissociation results in the elimination of neutral HCl. The ions H^+ are formed from the dissociation of CH_2Cl or CH_2Cl^+ and $H_2{}^+$ from CH_2Cl^+. The total energy is supplied for about four and five photons, respectively. In general, for CH_2X dissociation, theoretical calculations show that the barrier for the formation of $CH–H_2$ competes efficiently with C–X and C–H bond cleavage channels [19,20]. The ion H^+ results from single bond C–H dissociation, the most likely event under the favorable energy conditions, but the ion $H_2{}^+$ requires concerted double bond C–H dissociation in need of additional energy, five photons, becoming a nonfavorable process, evidenced in the low ion yield detected in our experiments.

3.2. *Trichloromethane*

In the $CHCl_3$ photodissociation spectra, see Fig. 1, resulting ions were identified as follow: high ion currents corresponding to H^+, C^+, CH^+, $^{35}Cl^+$, $^{37}Cl^+$, $C^{35}Cl^+$, and $C^{37}Cl^+$ ions, and very low ion currents of $H^{35}Cl^+$, $H^{37}Cl^+$, $CH^{35}Cl^+$, $CH^{37}Cl^+$, $CH^{35}Cl_2{}^+$, $CH^{35}Cl^{37}Cl^+$, and $CH^{37}Cl_2{}^+$ ions were detected. The absence of molecular parent ion indicates that photodissociation processes takes place previ-

Table 4
Dissociation and ionization energies reported for different fragments from chlorinated methanes.

Fragment	Products	Channel	Energy, eV	References
CH_2Cl	CH_2Cl^+	12	8.75	Ref. [31]
	$CH_2 + Cl$	13	3.79, 4.18	Ref. [19]
	$CHCl + H$	14	4.56, 4.72	Ref. [19]
	$CH + HCl$	15	3.98	Ref. [37]
CH_2Cl^+	$CCl^+ + H_2$	16	3.70	Ref. [19]
	$CHCl^+ + H$	17	4.99	Ref. [19]
	$CH_2{}^+ + Cl$	18	5.61	Ref. [19]
$CHCl_2$ $CHCl_2{}^+$	$CHCl_2{}^+$	19	8.32	Ref. [31]
	$CCl + HCl$	20	2.91	Ref. [20]
	$CHCl + Cl$	21	3.70, 3.81	Ref. [20]
	$CCl_2 + H$	22	4.05, 4.64	Ref. [20]
	$CH + Cl_2$	23	5.79	Ref. [20]
	$CCl^+ + HCl$	24	3.40	Ref. [20]
	$CHCl^+ + Cl$	25	4.44	Ref. [20]
	$CCl_2{}^+ + H$	26	4.75	Ref. [20]
	$CH^+ + Cl_2$	27	8.28	Ref. [20]
	$Cl_2{}^+ + CH$	28	8.98	Ref. [20]
CCl_3	$CCl_3{}^+$	29	8.11	Ref. [31]
	$CCl_2 + Cl$	30	2.89, 3.18	Ref. [34]
	$CCl + Cl_2$	31	–	–
$CHCl$	$CHCl^+$	32	9.84	Ref. [31]
$CHCl^+$	$CH^+ + Cl$	33	–	–
CCl_2	$CCl_2{}^+$	34	9.76	Ref. [31]
	$CCl^+ + Cl$	35	16.30	Ref. [31]
Cl_2	$Cl_2{}^+$	36	11.48	Ref. [31]
	$2Cl$	37	2.48	Refs. [36,37]
CCl	CCl^+	38	8.90	Ref. [31]
HCl	HCl^+	39	12.72	Ref. [31]
Cl	Cl^+	40	12.97	Ref. [31]

ously to the ionization. In several reports the structural stability of $CHCl_3^+$ has being discussed, and it is considered as an unstable species, producing different ions [20,26,27]. From our results we can conclude that the neutral molecule dissociates following one of the channels 5–8 reported in Table 3. Dissociative channel 5 is open when the molecule absorbs one photon of 355 nm, being favorable at low photon densities; channel 6 implies the absorption of two photons. Channels 7 and 8 are less likely because two atom elimination from neutral molecules is a more energetic process. Neutral radicals resulting from photodissociation processes have a residence time in the ionization region higher than ions, making possible the absorption of additional photons and their further ionization. From Table 2, it can be observed that the formation of $CHCl_2^+$ and CCl_3^+ requires three photons to produce the three-photon ionization of $CHCl_2$ and CCl_3 which are 8.16 and 8.11 eV, respectively. Sharma has reported some dissociative channels [20] which explain the result of photodissociation of $CHCl_2^+$ corresponding to the ions detected in our ToF spectra. These dissociative channels also explain the formation CCl^+, $CHCl^+$, CCl_2^+, CH^+, and Cl_2^+, channels 24–28 in Table 4, with 3.40, 4.44, 4.75, 8.28, and 8.98 eV dissociation energies, obtained by the *ab initio* calculations [20].

Ions resulting from channels 26 and 28 were no detected in our experiments; one mechanism [20] that can mediate the formation of these ions, takes into account the dissociation of neutral $CHCl_2$ to give a series of neutral species, channels 20–22. Such neutral species can undergo in further ionization by the absorption of additional number of photons. *Ab initio* calculations by Sharma et al. [20] indicate these channels, are accessible by the absorption of one or two photons. Considering the ionization potentials of each one of the neutral products, and the results shown in Table 2, we can interpret the results as follow: the HCl^+ can result by ionization of the neutral HCl absorbing four photons; also the ion $CHCl^+$ is the result of ionization of neutral radical CHCl absorbing three photons, CCl has a potential ionization of 8.9 eV which ionizes by three photon absorption also in good agreement with the calculated value by us. The excess of vibrational energy in the ionized state of the ions may result in attaining additional dissociative channels which can explain other low mass detected ions in the ToF spectra.

3.3. *Tretachloromethane*

In ToF spectra of CCl_4 the main ions detected correspond to C^+, $^{35}Cl^+$, $^{37}Cl^+$, $C^{35}Cl^+$, $C^{37}Cl^+$, and low yield of $C^{35}Cl_3^+$, $C^{35}Cl_2{}^{37}Cl^+$, $C^{35}Cl^{37}Cl_2^+$ and $C^{37}Cl_3^+$ was observed. The molecular parent ion is an unstable species which dissociates promptly. It was not detected in our experiments, indicating that photon absorption is followed by the molecular dissociation and ionization of the neutral fragments. The experimental bond dissociation energy for C–Cl from CCl_4 is about of 3.05 eV, which can be easy accessed by one photon absorption, channel 9 in Table 3.

Neutral CCl_3 and Cl are ionized and detected in the ToF spectra. From Table 4, we recognize that CCl_3^+ results from the three-photon absorption in good agreement with a 8.11 eV ionization energy, and a vibrational energy excess which can result in additional fast dissociation channels to give other ion products as CCl^+. Detection of Cl^+ in ToF spectra is probably originated in neutral Cl which is ionized by four photon absorption, see Table 2, this ion has an ionization potential of 12.97 eV, which is in good agreement with the present experimental results.

3.4. *Vibrational mediated photodissociation, VMP*

All the mechanisms discussed above can help to understanding the photodissociation of chlorinated methanes by single and multiple photon absorption. Depending on the isotopologue species, the result of differences in vibrational energy levels which mediates the photon absorption in the molecular electronic excited states for a particular compound was observed, Fig. 4. Changes in isotopic compositions modify the vibrational frequencies by some cm^{-1}. In Table 1, we report the calculated vibrational frequencies of possible isotopologues of chlorinated methanes in their ground electronic state. It can be observed that vibrations which involve chlorine atoms change by several cm^{-1} as a consequence of two stable chlorine isotopes. As it was mentioned before, these differences are considerable higher than the spectral width of 355 nm laser radiation used in our experiments. In some cases, the formation of daughter ions with identical atomic composition, show small differences of the number of absorbed photons, Table 2, or ion yield as can be seen in Fig. 4. If the photodissociation is mediated by resonant absorption through a C–Cl vibrational mode, the process is a *VMP*, and it can explain the enhanced ion yield observed in Fig. 4. This behavior can be interpreted on basis of resonant photon absorption which is mediated by vibrational energy levels. The effect of isotopologues on vibrational energy levels and resonant enhanced photons absorption is discussed below.

The presence of two stable isotopes, ^{35}Cl and ^{37}Cl, changes the molecular symmetry and also the molecular vibrational energy levels in both the ground and excited electronic states. In previous reports about CH_3Cl and CHD_2Cl dissociation, the formation of H and D ions was explained by a *VMP* mechanism [28,29]. From symmetry, only full symmetric vibrational modes (A_1) should be active. This allows a straightforward identification of the active modes. For the species of the highest symmetry, CH_4 and CCl_4 (T_d), this implies that only the C–H or C–Cl stretch (breathing) modes are allowed, whereas for species with lower symmetry, CH_3Cl ($C_{3\upsilon}$), CH_2Cl_2 ($C_{2\upsilon}$), and $CHCl_3$ ($C_{3\upsilon}$), more complicated vibrational structures involving combinations of C–H, C–Cl stretching and H–C–Cl, Cl–C–Cl, H–C–Cl bending modes are expected [5].

The two stable Cl isotopes, in the case of CH_2Cl_2, consist of an isotopic mixture of about 56% $CH_2{}^{35}Cl_2$, 38% $CH_2{}^{35}Cl^{37}Cl$, and 6% $CH_2{}^{37}Cl_2$, with molecular symmetries C_{2v}, C_s, and C_{2v}, respectively. For the C_{2v} symmetry isotopologues, this symmetry allows four vibrational modes of A_1 symmetry. Two of these vibrations are symmetric stretching modes: C–H (ν_1) and C–Cl (ν_3), and the other two are bending modes involving the H–C–H (ν_2) and Cl–C–Cl (ν_4) angles. The frequency values change due to chlorine isotopes difference in mass. In the case of C_s molecular symmetry, nine vibrational modes are allowed. Here, other vibrational frequencies correspond to asymmetric modes, and stretching C–Cl differences. In order to demonstrate the shift in vibrational frequencies due to the effect of the changes in isotopic composition, this shift was calculated using Density Functional Theory, within a B3LYP hybrid functional and a 6-311G (3df,2p) basis set, on software package Gaussian 03 [30]. The results do not consider the scaling factor for its basis set, Table 1.

From our experimental results, the ion yield ratios were calculated and shown in Fig. 4. The difference in natural abundance of ^{35}Cl and ^{37}Cl ratio close to 3:1 do not explain all the values obtained. For CH_2Cl_2, Fig. 3a, the main observed ions correspond to Cl^+ and CCl^+. The ratio $^{35}Cl/^{37}Cl$ maintains a constant value close to 3 within the experimental error indicating that the formation of this ion is not sensible to the vibrational structure of the isotopologues; in consequence the efficiency of the dissociation processes is not influenced by more than the natural isotopic abundance. In the same Fig. 4a, the calculated ratio $C^{35}Cl^+$ to $C^{37}Cl^+$ increases concomitantly with the pulse energy. As the formation of $C^{35}Cl^+$ is mediated by three photons; it can be originated from both neutral $CH_2{}^{35}Cl_2$ and $CH_2{}^{35}Cl^{37}Cl$.

Regarding three chlorine atoms halomethanes, trichloromethane, $CHCl_3$, consists of an isotopologues mixture of about 45% $CH^{35}Cl_3$, 42% $CH^{35}Cl_2{}^{37}Cl$, 13% $CH^{35}Cl^{37}Cl_2$,

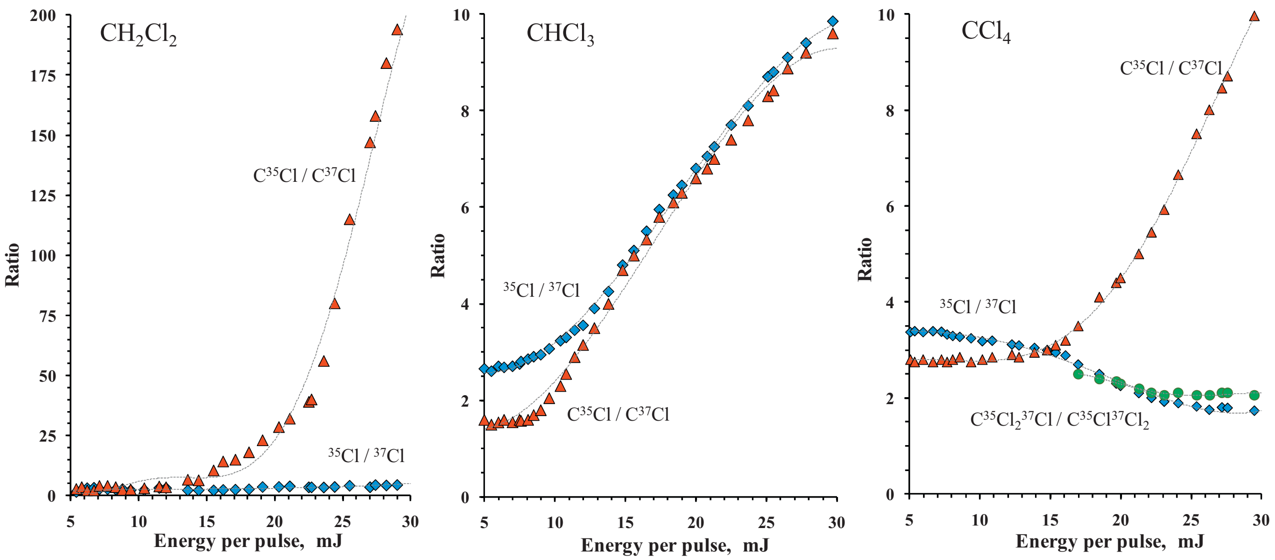

Fig. 4. Isotopologues ratios as a function of the energy per pulse.

and 1% $CH^{37}Cl_3$. Taking into account the isotopic distribution in reactant molecules we can assume the presence of two possible symmetries, the isotopologues $CH^{35}Cl_3$, and $CH^{37}Cl_3$ with a C_{3v} symmetry, while the other isotopologues, $CH^{35}Cl_2{}^{37}Cl$ and $CH^{35}Cl^{37}Cl_2$ with C_s symmetry. Changes in the vibrational frequencies can be observed as a consequence of symmetry, Table 1. Considering the two stable Cl isotopes in the case of C_{3v} symmetry, isotopologues vibrational frequency values are red shifted as the mass of the isotope increases. The C_s symmetry isotopologues result in an increase of the active modes. The changes in the C–Cl stretching and the Cl–C–Cl bending modes are remarkable: a behavior not observed when isotopes have equal mass, symmetry C_{3v}, Table 1. For the main observed ions in the photodissociation of $CHCl_3$, we calculated the isotopic ratios $^{35}Cl/^{37}Cl$ and $C^{35}Cl/C^{37}Cl$, Fig. 4b. It is observed that the ratio $^{35}Cl^+/^{37}Cl^+$ increases as the energy per pulse was increased. We can explain such effect by assuming that the formation of $^{35}Cl^+$ takes place in a dissociative process from an excited electronic state, which is related with a particular vibrational C–Cl mode, which is reached by the absorption of two photons at energies per pulse close to 10.7 mJ. A similar behavior occurs for the case of $C^{35}Cl^+/C^{37}Cl^+$, but the low energies per pulse for the $C^{37}Cl^+$ formation dominates over the other process with a ratio about three. In the other hand, high energies pulses dominates the $C^{35}Cl^+$ formation reaching a ratio close to three, as can be seen at maximum ion yield energies per pulse region (Fig. 4b). We interpreted these results as a consequence of the two vibrational mediated photodissociation processes.

In the case of tetrachloromethane, CCl_4, the isotopologues mixture of about 33% $C^{35}Cl_4$, 42% $C^{35}Cl_3{}^{37}Cl$, 20% $C^{35}Cl_2{}^{37}Cl_2$, 4.2% $C^{35}Cl^{37}Cl_3$, and 0.3% $C^{37}Cl_4$ is acknowledged. Table 1 shows the vibrational frequencies of the isotopologues for the isotopic composition. For cases of $C^{35}Cl_4$ and $C^{37}Cl_4$, they have T_d symmetry with only one active vibrational mode, the C–Cl stretching. For the $C^{35}Cl_2{}^{37}Cl_2$, it has symmetry C_{2v}, which shows four vibrational modes, and for two other isotopologues, $C^{35}Cl_3{}^{37}Cl$ and $C^{35}Cl^{37}Cl_3$, the symmetry corresponds to C_s. The effect of symmetry reveals the complexity of the vibrational structure that can be observed in the ground and excited states. In Fig. 4c the ion yield ratios of $^{35}Cl^+/^{37}Cl^+$, $C^{35}Cl^+/C^{37}Cl^+$, and $C^{35}Cl_2{}^{37}Cl^+/C^{35}Cl^{37}Cl_2{}^+$are shown, resulting from the photodissociation of CCl_4. The formation of the ion Cl^+, originated from four-photon absorption, and the formation of the isotope $^{37}Cl^+$ is enhanced as the energy per pulse is increased, vibrationally mediated, observing a decreasing in the isotope ratio. The ratio of $C^{35}Cl^+$ and $C^{37}Cl^+$ present an increasing in their value up to ten, at the energies per pulse used in our experiments. This indicates that the processes which lead to the $C^{35}Cl^+$ formation is mediated by either C–^{35}Cl or C–^{37}Cl bond strengths, depending of the isotopologue compound. Also the ions of the type $CCl_3{}^+$ come from the CCl_3 ionization and previous photodissociation of the neutral molecule. The observed behavior in the isotopologues ratio $C^{35}Cl_2{}^{37}Cl^+/C^{35}Cl^{37}Cl_2{}^+$ indicates that the formation of $C^{35}Cl_2{}^{37}Cl^+$ is vibrationally mediated and enhances its ion yield as the energy per pulse increases. This ion yield can be the result of a C–Cl bond breaking either $C^{35}Cl_2{}^{37}Cl_2$ or $C^{35}Cl_3{}^{37}Cl$ isotopologues, followed by the further elimination of an additional chlorine atom. If it takes place from $C^{35}Cl_2{}^{37}Cl_2$ the vibrational mediated process implies either a C–^{37}Cl bond strength or from $C^{35}Cl_3{}^{37}Cl$ it is related to C–^{35}Cl strength. Furthermore this process only occurs at energies per pulse higher than 16 mJ.

4. Conclusions

In this work we presented the results of the molecular photodissociation of chlorinated methanes, from two up to four chlorine atoms, performed by multiphoton absorption at 355 nm, and intensities from 10^9 up to 10^{10} W cm^{-2}. The processes were classified as dissociation–ionization, as the molecular parent ions were not observed. At the experimental conditions, processes which require up to four photons absorption were identified. According with the results, the type of ions produced and number of absorbed photons by the molecule, the main dissociation channels were proposed and compared with previous reports. The results indicate that the absorption of one photon can produce, in all the analyzed cases, the molecular dissociation results in neutral fragments which can absorb additional photons to produce ions, in the cases with an internal excess of vibrational energy and additional dissociation steps. Our results of calculated number of absorbed photons are in good agreement with previous reports of both experimental and theoretical results for the dissociation and ionization energies. The analysis of the ratios for ion yields between different isotopologues in chlorinated methanes reveals that the effect of the two chlorine isotopes, which exhibit different vibrational energy levels in ions and neutral compounds, promotes the dissociation processes which are vibrationally mediated. These vibrationally mediated photon absorptions, which modifies the efficiency of the dissociation processes, are being observed over all ion yields ratios and cannot be explained on the basis of natural abundances only. Finally, the isotopologue effect was observed for the vibrational energy levels all over the molecular neutral ground state, using Density Functional Theory with a B3LYP hybrid functional calculation. The energy levels are modified in accordance with the lighter chlorine isotopes replaced by the heavier isotopes.

Acknowledgements

Authors would like to thank the financial support of CONACYT, grant number 82521 and PAIIT-UNAM, grants IN108009 and IN 107-310, and the technical support of Mr. A. Gonzalez for his dedicated work to complete the experimental setup.

References

[1] W. Tsang, Mechanisms for the formation and destruction of chlorinated organic products of incomplete combustion, Combust. Sci. Technol. 74 (1990) 99–116.

[2] A.A. Viggiano, R.A. Morris, Ozone destruction by chlorine: the impracticality of mitigation through ion chemistry, Science 267 (1995) 82–84.

[3] B.R. Russell, L.O. Edwars, J.W. Raymonda, Vacuum ultraviolet absorption spectra of the chloromethanes, J. Am. Chem. Soc. 95 (1973) 2129–2133.

[4] T. Ogawa, I. Fujita, M. Hatada, K. Hirota, Emission spectra obtained by low energy electron bombardment of methane and chlorinated methanes, Bull. Chem. Soc. Jpn. 44 (1971) 659–662.

[5] S. Sundin, S.L. Saethre, A. Ausmees, S. Svensson, Vibrational structure of the chlorinated series, $CH_{4-n}Cl_n$, studied by core photoelectron spectroscopy and ab initio calculations, J. Chem. Phys. 110 (1999) 5806–5813.

[6] X. Yang, P. Felder, R. Huber, Photodissociation of the $CHFCl_2$ and $CHCl_3$ molecules and the $CHCl_2$ radical in a beam at 193 nm, Chem. Phys. 189 (1994) 127–136.

[7] R.A. Brownsword, M. Hillednkamp, Th. Laurent, R.K. Vatsa, H.-R. Volpp, J. Wolfrum, Dynamics of H atom formation in the photodissociation of chloromethanes at 193.3 nm, J. Phys. Chem. A 101 (1997) 5222–5227.

[8] A. Werner, B.P. Tsai, T. Baer, Photoionization study of the ionization potentials paths of the chlorinated methanes and carbon tetrabromide, J. Chem. Phys. 60 (1974) 3650–3657.

[9] S.-Y. Chiang, M. Bahou, K. Sankaran, Y.-P. Lee, H.-F. Lu, M.-D. Su, Dissociative photoionization of CH_2Cl_2 and enthalpy of formation of $CHCl^+$: experiments and calculations, J. Chem. Phys. 118 (2003) 62–69.

[10] D.P. Seccombe, R.P. Tuckett, H. Baumgärtel, H.W. Jochims, Vacuum-UV fluorescence spectroscopy of CCl_3F, CCl_3H and CCl_3Br in the range 8–30 eV, Phys. Chem. Chem. Phys. 1 (1999) 773–782.

[11] H.K. Haak, F. Stuhl, VUV fluorescence from the UV-multiphoton dissociation of chlorinated methanes, Chem. Phys. Lett. 68 (1979) 399–402.

[12] V.R. Bhardwaj, F.A. Rajgara, K. Vijayalakshmi, V. Kumarappan, D. Mathur, Dissociative ionization of gas-phase chloromethanes by intense fields of picoseconds and attosecond duration, Phys. Rev. A 58 (1998) 3849–3855.

[13] G.R. Long, J.W. Hudgens, Resonance enhanced multiphoton ionization spectroscopy of $CHCl_2$ and $CDCl_2$, J. Phys. Chem. 91 (1987) 5870–5872.

[14] J.W. Hudgens, G.R. Long, Resonance-enhanced multiphoton ionization spectroscopy of $CHCl_2$ and $CDCl_2$, AIP Conf. Proc. 172 (1988) 337–339.

[15] B.S. Jursic, J.W. Timberlake, Computation of bond dissociation energies of substituted methanes with density functional theory, Tetrahedron Lett. 37 (1996) 6473–6474.

[16] B.S. Jursic, C–H and C-halogenated bond dissociation energies for fluorinated and chlorinated methane evaluated with hybrid B3LYP density functional theory methods and their comparison with experimental data and the CBS-Q ab initio computational approach, J. Mol. Struct. (Theochem) 422 (1998) 253–257.

[17] F.B. Brown, D.G. Truhlar, Dissociation potential for breaking a C–H bond in methane, Chem. Phys. Lett. 113 (1985) 441–446.

[18] R.J. Duchovic, W.L. Hase, S.H. Bernhard, M.J. Frisch, K. Raghavachari, Ab initio potential energy curve for CH bond dissociation in methane, Chem. Phys. Lett. 89 (1982) 120–125.

[19] P. Sharma, R.K. Vatsa, D.K. Maity, S.K. Kulshreshtha, Laser induced photodissociation of CH_2Cl_2 and CH_2Br_2 at 355 nm: an experimental and theoretical study, Chem. Phys. Lett. 382 (2003) 637–643.

[20] P. Sharma, R.K. Vatsa, D.K. Maity, S.K. Kulshreshtha, Multiphoton dissociation/ionization of $CHCl_3$ and $CFCl_3$ at 355 nm: an experimental and theoretical study, Rapid Commun. Mass Spectrom. 18 (2004) 2383–2387.

[21] H. Sato, Photodissociation of simple molecules in the gas phase, Chem. Rev. 101 (2001) 2687–2725.

[22] R.I. Vander Wal, F.F. Crim, Controlling the pathways in molecular decomposition: the vibrational mediated photodissociation of water, J. Phys. Chem. 93 (1989) 5331–5333.

[23] Rh.J. Barnes, A.F. Gross, A. Sinha, Accessing highly vibrationally excited states of water using double resonance vibrationally mediated photodissociation, J. Chem. Phys. 106 (1997) 1284–1287.

[24] Ch. Tao, P.J. Dagdigian, Vibrationally mediated photodissociation of CH_3Cl: the $\nu=3$ and 4 CH stretch overtone levels, Chem. Phys. Lett. 350 (2001) 63–70.

[25] E. Mejia-Ospino, I. Álvarez, C. Cisneros, Opo-time of flight system for multiphoton ionization and dissociation studies, Rev. Mex. Fís. 50 (2004) 170–178.

[26] D. Mathur, K. Vijayalaksmi, Angle-resolved mass spectrometry of chloromethanes in an intense laser field, Rapid Commun. Mass Spectrom. 12 (1998) 246–250.

[27] V.R. Bharwaj, F.A. Rajgara, K. Vijaylakshimi, V. Kumarapan, D. Mathur, A.K. Sinha, Dissociative ionization of gas-phase chloromethanes by intense fields of picosecond and attosecond duration, Phys. Rev. A 58 (1998) 3849–3855.

[28] H.M. Lambert, P.J. Dagdigian, Photodissociation of vibrational excited CH_3Cl: modification of the dissociation dynamics, Chem. Phys. Lett. 275 (1997) 499–505.

[29] H.M. Lambert, P.J. Dagdigian, Photodissociation of CH stretch overtone excited CH_3Cl and CHD_2Cl ($v_{CH} = 5$): Cl spin-orbit branching and atomic fragment yields, J. Chem. Phys. 109 (1998) 7810–7820.

[30] M.J. Frisch, et al., Gaussian 03, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 2003.

[31] NIST Chemistry Webbook, available: http://webbook.nist.gov/chemistry.

[32] R. Marom, A. Golan, S. Rosenwaks, I. Bar, Photodissociation dynamics of vibrationally excited CH_2Cl_2 molecules, Chem. Phys. Lett. 378 (2003) 305–312;
R. Marom, A. Golan, S. Rosenwaks, I. Bar, Intramolecular dynamics in the photofragmentation of initially vibrationally excited CH_2Cl_2, J. Phys. Chem. A 108 (2004) 8089–8095.

[33] H. Biehla, K.J. Boylea, D.P. Seccombea, D.M. Smitha, R.P. Tucketta, H. Baumgärtelb, H.W. Jochims, Vacuum–UV fluorescence spectroscopy of CCl_4, $SiCl_4$ and $GeCl_4$ in the range 9–25 eV, J. Electron. Spectrosc. Relat. Phenom. 97 (1998) 89–113.

[34] Q. Li, Q. Ran, C. Chen, Sh. Yu, X. Ma, L. Sheng, Y. Zhang, W.-K. Li, Experimental and theoretical study of the photoionization and dissociative photoionization of carbon tetrachloride, Int. J. Mass Spectrom. Ion Processes 153 (1996) 29–36.

[35] A. Hank, A. Läuter, H.-R. Volpp, Absolute chlorine atom quantum yield measurements in the UV and VUV gas-phase laser photolysis of CCl_4, Chem. Phys. Lett. 368 (2003) 445–451.

[36] J. Li, Y. Hao, J. Yang, C. Zhou, Y. Moa, Vibrational structure, spin-orbit splitting, and bond dissociation energy of $Cl_2^+(X^2\pi_g)$ studied by zero kinetic energy photoelectron spectroscopy and ion-pair formation imaging method, J. Chem. Phys. 127 (2007) 1043071–1043078.

[37] V. Dribinski, A.B. Potter, A.V. Demyanenko, H. Reisler, Photodissociation dynamics of the CH_2Cl radical: ion imaging studies of the Cl–CH_2 channel, J. Chem. Phys. 115 (2001) 7474–7484.