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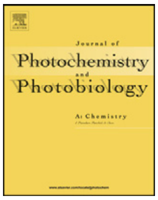

Multiphoton dissociation and vibrational mediated dissociation of chlorinated methanes, $CH_{4-n}Cl_n$ ($n = 2, 3, 4$) at 355 nm

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

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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-

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

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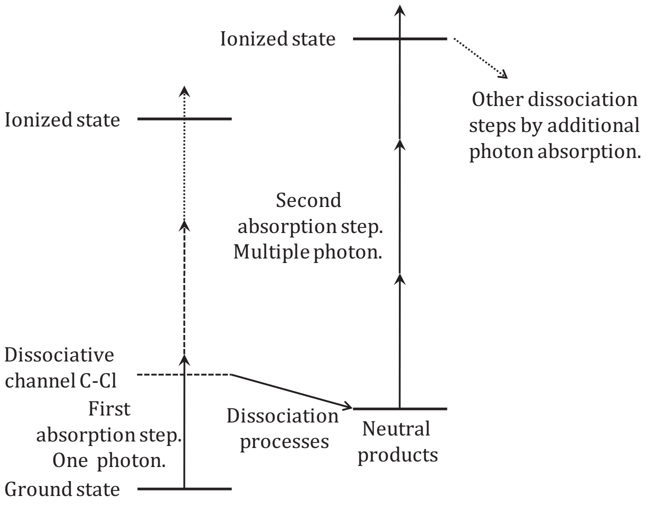

Fig. 1. Photodissociation–photoionization mechanism in chlorinated methanes.

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 5×10^{10} 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.