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Is spin-orbit state branching in the photodissociation of CCl_4 isotope specific?

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Abstract

We have reinvestigated the ultraviolet photodissociation of CCl_4 around 235 nm. The yield of spin-orbit state excited $Cl^*(^2P_{1/2})$ atoms was found to be 0.26 ± 0.03, independently of the isotopic mass of the chlorine atom. No evidence of isotope specific Cl* yields was observed. Our results suggest that the previously reported isotope specificity in the photodissociation of CCl_4 does not exist.

Keywords: Photodissociation; Spin-orbit state branching; Carbon tetra chloride

Recently, the chemical properties of electronically excited halogen atoms have extensively been reviewed [1]. One common experimental approach for generating electronically excited halogen atoms is the photodissociation of suitable precursor molecules. Normally, for these processes one would not expect any pronounced isotope specific behavior for spin-orbit state branching ratios of the halogen atom photofragment because electronic photoexcitation is independent of the isotopic composition of the precursor and the mass difference of the fragment isotopes is too small to be significant in tunneling processes. In fact, except for one case no such behavior has been reported in the literature.

The one exception was published in 1994 by Deshmukh and Hess who reported isotope specific branching ratios in the ultraviolet photodissociation of CCl_4 [2]. They used a single laser for dissociation of the jet-cooled CCl_4 precursor and for the detection of the chlorine atoms by (2 + 1) resonance enhanced multi-photon ionization (REMPI). Electronically excited Cl* atoms were probed via the $^2D_{3/2}{}^o \leftarrow {}^2P_{1/2}{}^o$ transition at 237.79 nm, and ground state Cl atoms were probed via the $^2D_{3/2}{}^o \leftarrow {}^2P_{3/2}{}^o$ transition at 235.33 nm and via the $^4D_{5/2}{}^o \leftarrow {}^2P_{3/2}{}^o$ transition at 237.72 nm, respectively, and monitored by a double-stage multichannel plate (MCP) assembly [3]. Isotope specific Cl* yields of $\Gamma_1 = P(^{35}Cl^*)/[P(^{35}Cl) + P(^{35}Cl^*)] = 0.20 \pm 0.02$ and $\Gamma_2 = P(^{37}Cl^*)/[P(^{37}Cl) + P(^{37}Cl^*)] = 0.44 \pm 0.03$ were reported without attempting an interpretation of this surprising observation [2]. P is the number of observed atoms for a given mass in a given quantum state. Based on these data, one arrives at the following normalized, isotope and state specific fragment yields α_{ij}:

$$\alpha_{11} = \frac{\rho_0}{\rho_0+1}(1-\Gamma_1), \qquad \alpha_{12} = \frac{\rho_0}{\rho_0+1}\Gamma_1 \tag{1a}$$

$$\alpha_{21} = \frac{1}{\rho_0+1}(1-\Gamma_2), \qquad \alpha_{22} = \frac{1}{\rho_0+1}\Gamma_2 \tag{1b}$$

Here, the index $i = 1, 2$ denotes the isotopic masses 35 and 37, respectively, while $j = 1, 2$ denotes the spin-orbit states $^2P_{3/2}$ and $^2P_{1/2}$, respectively. $\rho_0 = [P(^{35}Cl) + P(^{35}Cl^*)]/[P(^{37}Cl) + P(^{37}Cl^*)] = 3.12 \pm 0.02$ [4] is the natural isotopic distribution. α_{ij} values calculated from Eq. (1) are listed in Table 1.

In their experiment isotope separation was achieved in a linear time-of-flight spectrometer. Cl* yields were calculated from integrated ion signals for wavelength scans over the respective atomic transitions. This method relies on the independence of the signal intensities of the two chlorine isotopes from each other, a prerequisite which is likely not to be fulfilled if the ^{35}Cl signal of a strong the chlorine atom transition exceeds a limiting value where saturation of the MCP detector assembly sets in. On the other hand, signal intensities cannot freely be chosen because the laser intensity needs to be held con-

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Table 1
Normalized isotope specific spin-orbit state yields α_{ij} calculated from the Γ_i values reported by Deshmukh and Hess [2]

	Γ_i	$^2P_{3/2}$ ($j=1$)	$^2P_{1/2}$ ($j=2$)
^{35}Cl ($i=1$)	0.20 ± 0.02	0.606	0.151
^{37}Cl ($i=2$)	0.44 ± 0.03	0.136	0.107
ρ_j		4.46	1.41

The bottom row contains state specific isotope ratios $\rho_j = \alpha_{1j}/\alpha_{2j}$ predicted from the data of ref. [2].

Table 2
Chlorine atom two-photon 4p–3p transitions employed in this work and observed state specific isotope ratios ρ_j

No.	Probed state	Upper state	Wavelength (nm)	Isotope ratio, ρ
1	Cl($^2P_{3/2}$)	$^2P_{3/2}$	234.08	2.97
2	Cl*($^2P_{1/2}$)	$^2P_{1/2}$	235.20	3.20
3	Cl($^2P_{3/2}$)	$^2D_{3/2}$	235.33	3.00
4	Cl*($^2P_{1/2}$)	$^2S_{1/2}$	237.07	3.00
5	Cl($^2P_{3/2}$)	$^2D_{5/2}$	237.72	2.93

stant for different transitions in order to be comparable to each other.

For this reason we have decided to repeat the experiment of ref. [2] under slightly changed experimental conditions. Instead of trying to determine isotope specific Cl* yields Γ_i – based on cell values in the same row in Table 1 – we have measured state specific isotope ratios ρ_j which are given by the corresponding "vertical" ratios of cells in the same column in Table 1: $\rho_j = \alpha_{1j}/\alpha_{2j}$. To this end we had only to determine the area ratio for selected transitions of ground state Cl and excited spin-orbit state Cl* atoms. The advantage of this approach is that the laser intensity can be adjusted to the signal intensity in order to assure saturation free conditions for the MCP detector.

We have employed a simplified version of an experimental setup which has been described in detail before [5]. Briefly, it consists of a home-built single-field time-of-flight (TOF) spectrometer with a total length of 0.57 m and a ratio of the acceleration region to the drift region of 1:2 which could be evacuated to a base pressure of 10^{-4} Pa. Pure CCl_4 without further purification was fed into the spectrometer via a needle valve resulting in typical sample pressures of 10^{-2} Pa. Simultaneous dissociation of CCl_4 and state-selective detection of chlorine atoms was performed using a dye laser pumped by an excimer laser (Lambda Physik LPD 3000, Lambda Physik LPX 605i). The dye laser was operated with Coumarin 47 at a repetition rate of 10 Hz, its light was frequency doubled by a BBO crystal and focused into the spectrometer by a 60 mm quartz lens.

The dissociation energy for the dissociation

$$CCl_4 + h\nu \rightarrow CCl_3 + Cl \qquad (2)$$

is calculated to be 293.5 ± 10 kJ/mol [6], resulting in an available energy of 215.6 ± 10 kJ/mol at a dissociation wavelength of 235 nm. Thus, the maximum speed for ^{35}Cl fragments is 3070 ± 80 m/s.

In order to observe well separated mass peaks for ^{35}Cl and ^{37}Cl isotopes the acceleration field strength was set to 10^4 V/m resulting in times of flight of 7.5 μs for ^{35}Cl and 7.7 μs for ^{37}Cl. For these conditions, the maximum profile broadening due to the kinetic energy release in the dissociation process, corresponding to the maximum speed of 3070 m/s, is calculated to be 226 ± 6 ns [7]. The experimentally observed profiles are somewhat narrower than the maximum value, indicating significant internal excitation of the CCl_3 partner fragment.

The laser intensity was typically kept at or below 500 μJ per pulse, owing to the relatively small CCl_4 absorption cross section of 1.1×10^{-20} cm^2 to 1.8×10^{-20} cm^2 in the 238 nm to 235 nm wavelength range [8]. Non-negligible non-resonant background signal from residual gas and pumping oil was accounted for by subtracting profiles obtained without sample from the sample spectra. Generally, background corrected profiles exhibited a smooth and unstructured baseline which proves the absence of detector saturation. Also, due to the small absorption cross sections, distortion of the TOF profiles due to space charge effects was negligible. Moreover, it is not an issue for this kind of experiments since only the shape of the profiles would be affected, but not the integrated area.

Chlorine atoms in both spin-orbit states were resonantly ionized employing a (2 + 1)-REMPI scheme via the five transitions

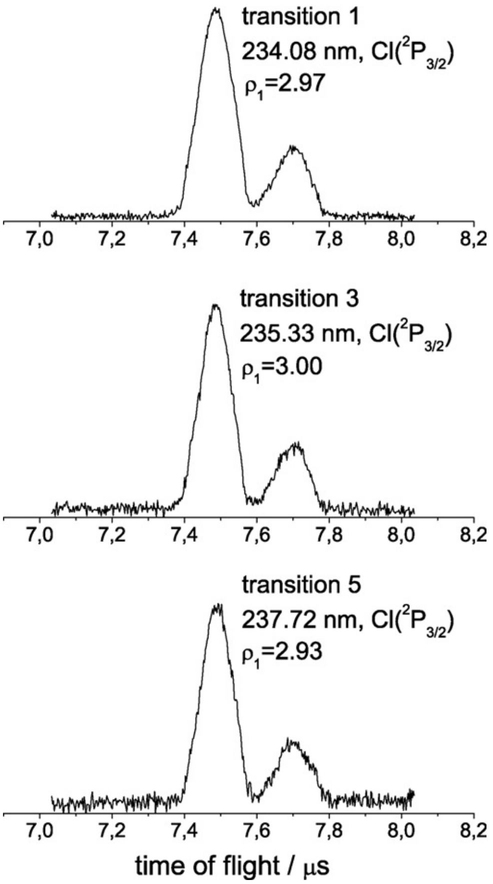

Fig. 1. Time-of-flight profiles for transitions 1, 3, and 5 originating from ground state ^{35}Cl($^2P_{3/2}$) (left peak) and ^{37}Cl($^2P_{3/2}$) (right peak). Profiles have been corrected for non-resonant background signal and scaled to equal amplitudes of the ^{35}Cl isotope. The state specific isotope ratios ρ_1 have been calculated as the ratios of the peak areas.

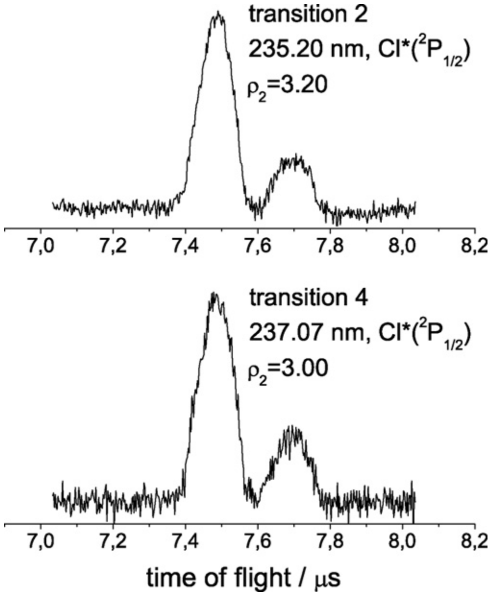

Fig. 2. Time-of-flight profiles for transitions 2 and 4 originating from spin-orbit excited state $^{35}Cl^*(^2P_{1/2})$ (left peak) and $^{37}Cl^*(^2P_{1/2})$ (right peak). Profiles have been corrected for non-resonant background signal and scaled to equal amplitudes of the ^{35}Cl isotope. The state specific isotope ratios ρ_2 have been calculated as the ratios of the peak areas.

listed in Table 2. The ions were detected by a double stage multichannel plate assembly with 40 mm active diameter. The ion signal was monitored by a digital transient wave form recorder (LeCroy 9450).

The background corrected time-of-flight profiles for ground state $Cl(^2P_{3/2})$, observed for the transitions 1, 3, and 5 of Table 2 are shown in Fig. 1. In Fig. 2, the corresponding profiles are presented for transitions 2 and 4, originating from spin-orbit excited $Cl^*(^2P_{1/2})$.

The attempt to monitor a third, strong transition for spin-orbit excited $Cl^*(^2P_{1/2})$ failed because of the limited tuning range of the Coumarin 47 laser dye. Nevertheless, the investigated five transitions, three for ground state $Cl(^2P_{3/2})$ and two for spin-orbit excited $Cl^*(^2P_{1/2})$ clearly do not show the behavior expected from the previous experiments by Deshmukh and Hess. On the contrary, within experimental error state specific isotope ratios match the natural abundance in every single case.

As to the source of their error we can only speculate since not all data necessary to completely characterize their experiment have been published. Nevertheless, we believe it to be likely that detector saturation effects have affected the measurements. In an attempt to reproduce the behavior observed by Deshmukh and Hess, we have repeated their experiment for transitions 2 and 3 with different MCP voltages and received signal intensity ratios $I(^{35}Cl)/I^*(^{35}Cl)$ between 3.02 for small MCP voltages and 2.42 for large MCP voltages, respectively.

In order to quantify the Cl* yield we have used the low voltage values of the signal intensity ratios since they were obtained unaffected from detector saturation. Taking into account the oscillator strength ratio $f(Cl)/f(Cl^*) = 1.06 \pm 0.17$ [9], the population ratio $P(Cl)/P(Cl^*)$ is given by the product $I(Cl)/I(Cl^*) \times f(Cl^*)/f(Cl)$ which is equal to $3.02/1.06 = 2.83 \pm 0.45$. Thus, $\Gamma(Cl^*) = 1/3.83 = 0.26 \pm 0.03$.

In summary, we have demonstrated that the Cl* yield $\Gamma = 0.26 \pm 0.03$ for both ^{35}Cl and ^{37}Cl isotopes. Consequently, we conclude that the Cl* yield in the UV photodissociation of CCl_4 is not isotope specific, and the previously published values of Deshmukh and Hess must be regarded as erroneous.

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