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# Photodissociation of the Trichloromethyl Radical: Photofragment Imaging and Femtosecond Photoelectron Spectroscopy

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Halogen-containing radicals play a key role in catalytic reactions leading to stratospheric ozone destruction, thus their photochemistry is of considerable interest. Here we investigate the photodissociation dynamics of the trichloromethyl radical,  $\text{CCl}_3$  after excitation in the ultraviolet. While the primary processes directly after light absorption are followed by femtosecond-time resolved photoionisation and photoelectron spectroscopy, the reaction products are monitored by photofragment imaging using nanosecond-lasers. The dominant reaction is loss of a Cl atom, associated with a  $\text{CCl}_2$  fragment. However, the detection of Cl atoms is of limited value, because in the pyrolysis  $\text{CCl}_2$  is formed as a side product, which in turn dissociates to  $\text{CCl} + \text{Cl}$ . We therefore additionally monitored the molecular fragments  $\text{CCl}_2$  and  $\text{CCl}$  by photoionisation at 118.2 nm and disentangled the contributions from various processes. A comparison of the  $\text{CCl}$  images with control experiments on  $\text{CCl}_2$  suggest that the dissociation to  $\text{CCl} + \text{Cl}_2$  contributes to the photochemistry of  $\text{CCl}_3$ .

## A Introduction

The photochemistry of halogen-containing species has gained considerable interest since the discovery of their role in the destruction of stratospheric ozone.<sup>1</sup> Numerous alkyl and alkenyl halides, in particular chlorine-substituted have thus been investigated in the gas phase over the years to obtain UV photoabsorption and photodissociation cross sections, but also photodissociation products and branching ratios.<sup>2-9</sup> In contrast, much less is known about open-shell species, i.e. chloroalkyl radicals. Diatomics CX (X=F, Cl, Br, I) have been investigated by high-resolution spectroscopy and their excited states were characterized in detail.<sup>10, 11</sup> The electronic spectroscopy of  $\text{CCl}_2$  has been studied in matrix<sup>12</sup> as well as in the gas phase.<sup>13, 14</sup> The photodissociation of  $\text{CCl}_2$  to  $\text{CCl} + \text{Cl}$  has been explored by the Dagdigian group using laser-induced fluorescence, who reported both the spin-orbit branching ratio of Cl as well as a bimodal rotational state distribution of  $\text{CCl}$ ,<sup>15-17</sup> and by Huber and coworkers, who applied photofragment translational spectroscopy.<sup>18</sup> Also the excited states of mixed carbenes  $\text{CXY}$  were characterized by high resolution electronic spectroscopy.<sup>19-22</sup>

Here we focus on the trichloromethyl radical,  $\text{CCl}_3$ , which appears as an intermediate in the photodissociation of chloroalkanes and -alkenes in the upper atmosphere,<sup>23, 24</sup> compounds that are involved in stratospheric ozone depletion. The kinetics of the  $\text{CCl}_3 + \text{O}_2$  reaction has also been monitored because of its relevance in plasma etching.<sup>25-27</sup> UV absorption and multiphoton ionisation (MPI) yielded information on two-photon excited Rydberg states.<sup>28</sup> Danis et al. identified a structureless band with maximum absorption at 210 nm and an absorption cross section  $\sigma_{\text{abs}} = 14.5 \text{ Mb}$ .<sup>29</sup> This band was later assigned to the transition from the  $X \ ^2A_1$  ground state into the  $C \ ^2A_1'$  (3s) Rydberg state.<sup>30</sup> Partial resolution of the out-of-plane bending mode and absorption cross sections  $\sigma_{\text{abs}}$  at the band heads ranging from 10.2 Mb at 224.8 nm to 1.7 Mb at 250.5 nm were reported, in qualitative agreement with the previous work. An accurate ionisation energy (IE) of 8.06 eV as well as information on the ionic ground state was obtained from a vibrationally resolved photoelectron spectrum.<sup>31</sup> While the neutral ground state is pyramidal ( $C_{3v}$ ) the ionic ground state is planar ( $D_{3h}$ ). However, the excited state dynamics has been scarcely explored. The only experimental study of Hintsä et al. used translational energy spectroscopy to explore the photodissociation at 308 nm.<sup>32</sup> In this work, only loss of chlorine was found, thus the dominant photodissociation pathway is  $\text{CCl}_3 \rightarrow \text{CCl}_2 + \text{Cl}$ . Hintsä et al reported an average translational energy release of  $13 \text{ kcal}\cdot\text{mol}^{-1}$  ( $54 \text{ kJ}\cdot\text{mol}^{-1}$ ) and an anisotropy parameter  $\beta \approx 1 \pm 0.2$ . Computationally, the neutral and ionic ground state have been investigated,<sup>31, 33</sup> but information available on the excited electronic states is limited to low-level methods like Hartree-Fock.<sup>28</sup> In order to obtain a full picture of the excited-state dynamics of  $\text{CCl}_3$ , we initiated a study that combines femtosecond-time resolved photoionisation and photoelectron spectroscopy (TR-PES)<sup>34-36</sup> to explore the initial processes following photoexcitation with nanosecond photofragment imaging<sup>37, 38</sup> to

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monitor the photodissociation products. The latter approach has evolved into a method that provides detailed insight into the photodissociation mechanism of stable molecules<sup>38-40</sup> and radicals<sup>41</sup> by monitoring the translational energy release of photofragments. In the past, we applied the method to investigate H-atom loss from radicals,<sup>42</sup> biradicals<sup>43</sup> and carbenes,<sup>44</sup> but recently extended our work to chlorine-containing molecules.<sup>45</sup> Experiments are accompanied by computations using time-dependent density functional theory (TD-DFT).

## B Experimental

$\text{CCl}_3$  was generated by flash pyrolysis either from  $\text{CCl}_3\text{Br}$  or from  $\text{CCl}_4$ . In addition,  $\text{CHCl}_3$  (chloroform) was employed for control experiments on  $\text{CCl}_2$ . All precursors were commercially obtained from Sigma-Aldrich, seeded in around 1.5 - 2 bar of Ar and thermally cleaved in an electrically heated SiC tube, mounted on a solenoid pulsed valve. In the subsequent adiabatic expansion, the radicals are typically cooled to vibrational temperatures of 150 K, as concluded from previous work.<sup>43</sup>

In both, the femtosecond (fs-) time resolved experiments and the nanosecond (ns-) photofragment detection, the velocity map imaging (VMI) technique was applied.<sup>37, 38</sup> Fs-time resolved experiments were conducted at the LUCA/SLIC laser facility. Photoelectron images (PEI) were recorded and yielded the TR-PES. Experimental conditions were similar to previous experiments.<sup>46, 47</sup> Briefly, the tripled fundamental of the Ti:Sa laser around 266 nm (10-50  $\mu\text{J}$ ) was used as the pump pulse, for the probe pulse the fundamental of the Ti:Sa laser (798 nm, 0.1-0.7 mJ) was employed. For the time-resolved mass spectra six scans were averaged, for the photoelectron images seven scans. Within one scan the ion signal as well as the PE images were integrated over 150 laser shots. As no dependence on the relative polarisation of the pump and probe pulses was observed, the rotational mean is discussed in the experimental spectra. The one-colour background signal was subtracted from the delay traces. The ns-experiments were conducted at the University of Würzburg, using a photofragment imaging setup.<sup>42, 45</sup> A skimmed free molecular jet enters the time of flight mass spectrometer (TOF-MS), which can be operated in either space-focusing or VMI configuration. Two separate counterpropagating ns-laser systems were used to dissociate and ionize the fragments. For photodissociation, the unfocused frequency-doubled output of a Nd:YAG laser pumped dye laser (230 nm – 250 nm/5.39 eV - 4.96 eV) with 0.5-1.0 mJ/pulse was used, polarized parallel to the detector plane. For ionisation we either employed the 9<sup>th</sup> harmonic of a Nd-YAG laser at 118.2 nm for the molecular fragments or a second tuneable dye laser system for ionisation of Cl atoms in a [1+1'] resonance-enhanced MPI process. In the latter, the  ${}^2\text{D}_{5/2} \leftarrow {}^2\text{P}_{3/2}^{\text{O}}$  transition of Cl was excited by 118.9 nm radiation, produced by frequency tripling the second harmonic output of a second dye laser system in Xe. Note that the spin-orbit excited  ${}^2\text{P}_{1/2}$  state of Cl cannot be probed by this scheme, as discussed previously, because there is no suitable transition in the tripling range accessible with the setup.<sup>45</sup>

For these experiments, the dye laser was scanned over the entire Doppler profile of the atomic transition. The residual 356.7 nm light was employed for the ionisation step.<sup>45</sup> The velocity map images were accumulated over  $10^4$  laser shots and one-colour background was subtracted. Mass spectra were recorded by monitoring the current generated upon ion impact on the MCPs. Further details on the ion optics, the imaging detector and the laser systems are given in the ESI.

In both fs-PEI and ns-photofragment imaging, the 3D Newton sphere was reconstructed from the image via inverse Abel transformation with the pBASEX algorithm, employing Legendre polynomials up to the 4<sup>th</sup> order.<sup>48</sup> From this reconstruction, the photoelectron spectra (fs-experiments) and the translational energy release distributions  $P(E_T)$  (ns-experiments) were derived.

Calculations were performed using DFT (density functional theory) employing the Qchem4 package, the CAM-B3LYP functional and the aug-cc-pVTZ basis set.<sup>49</sup> Excited states were calculated using TD-DFT, also employing the CAM-B3LYP functional and the aug-cc-pVTZ basis set. TD-DFT is rather simple and inexpensive method that nevertheless yields reasonably accurate vertical excitation energies for many radicals.<sup>50</sup> Spin contamination can be problematic, but were negligible in the computations presented below. For all calculated states,  $S^2$  was around 0.8 at most, with a nominal value of 0.75.

## C Results

### Calculations

The  $\text{CCl}_3$  radical is  $\text{C}_{3v}$ -symmetric with a  $X^2\text{A}_1$  electronic ground state. For the optimized ground state structure, we find a C-Cl bond length  $R_{\text{C-Cl}} = 1.708 \text{ \AA}$ , and angles  $\alpha_{\text{Cl-C-Cl}} = 117.3^\circ$  and  $d_{\text{Cl-C-Cl-Cl}} = -148.0^\circ$ , in agreement with previous work.<sup>31</sup> The singly occupied molecular orbital (SOMO) can be seen in a first approximation as a  $p$ -orbital centred at the carbon atom, with contributions from the non-bonding orbitals at the chlorine. The relevant excited states, as well as vertical excitation energies and oscillator strengths for transitions from the ground state, as well as an approximate character of the transition are given in Table 1.

Table 1: Vertical excitation energies (at the ground state minimum geometry) and oscillator strengths  $f$ , computed by TD-DFT.

State	$E_{\text{vert}} / \text{eV}$	Osc. Strength $f$	Attribution
$2^2\text{A}_1$	3.80	$9.1 \cdot 10^{-5}$	SOMO $\rightarrow$ LUMO, (C-Cl antibonding)
$1^2\text{A}_2$	4.96	0	$n_{\text{Cl}} \rightarrow$ SOMO
$1^2\text{E}$	5.41	$4.1 \cdot 10^{-5}$	SOMO $\rightarrow$ 3p-Rydberg/ HOMO-2 $\rightarrow$ SOMO
$2^2\text{E}$	5.69	$4.2 \cdot 10^{-2}$	HOMO-2 $\rightarrow$ SOMO
$3^2\text{A}_1$	5.74	$1.3 \cdot 10^{-2}$	SOMO $\rightarrow$ 3s-Rydberg

The transition into the lowest-lying excited state is centred in the near UV at 3.80 eV, corresponding to 326 nm. With an oscillator strength  $f$  around  $10^{-4}$  it is expected to be rather weak. The second excited state is of  $A_2$  symmetry, thus transitions from the ground state are dipole-forbidden. Above 5 eV a number of close-lying excited states are computed, two of them with considerable Rydberg character. Due to their energetic proximity the states are expected to be strongly coupled. Transitions into the  $1^2E$  state are again expected to be rather weak. The next states, the  $2^2E$  and the  $3^2A_1(3s)$  state are associated with  $f=0.1-0.01$  and thus provide the absorption strength for excitation in the far-UV. In previous work an absorption band was observed that sets in around 270 nm and maximises at 210 nm, corresponding to  $E_{\text{vert}}=5.90$  eV. It has been assigned to the  $3^2A_1(3s)$  state ( ${}^2A_1'$  in  $D_{3h}$ ).<sup>30</sup> The computed transition dipole moment  $\mu_T$  is oriented along the symmetry axis of the radical. Based on our computations, the  $2^2E$  will also contribute to this band. Here,  $\mu_T$  is perpendicular to the symmetry axis. From a comparison with the experimental work we conclude that the computed  $E_{\text{vert}}$  are accurate to within  $\pm 0.2$  eV.

### Mass Spectra

Figure 1a) shows the two-colour photoionisation mass spectrum (PIMS) of pyrolysed  $\text{CCl}_4$  with 230 nm excitation and 118.2 nm ionisation (black line). Note that  $\text{CCl}_4$  has an IE of 11.47 eV, thus no signal was observed without pyrolysis. A power of 40 W was applied to the SiC tube, corresponding to roughly 700 - 800 K. The main pyrolysis product is  $\text{CCl}_3$  ( $m/z = 117-123$ ), contributions from  $\text{CCl}_2$  ( $m/z$  82-86) and  $\text{CCl}$  (47, 49) are also identified. Minute amounts of  $\text{C}_2\text{Cl}_2$  ( $m/z$  94- 98),  $\text{C}_2\text{Cl}_3$  ( $m/z$  129-135) and  $\text{C}_2\text{Cl}_4$  ( $m/z$  164- 172) can also be observed. Close ups of the relevant contributions  $\text{CCl}$ ,  $\text{CCl}_2$  and  $\text{CCl}_3$  are shown in Figure 1b), c) and d). The red and blue curves represent the signals with only ionisation or dissociation laser present. Upon turning the dissociation laser on, the  $\text{CCl}$  and  $\text{CCl}_2$  signals increase roughly by a factor of two (black curve), indicating that they are formed in the dissociation, while the  $\text{CCl}_3$  signal stays constant within the accuracy of the experiment. Also, one-colour ionisation of  $\text{CCl}$  by the 230 nm radiation is visible. Due to the delay between the two lasers, the peak appears at earlier time-of-flight, corresponding to  $m/z$  38 and 40 for the two-colour signal. PIMS were also recorded at 235 nm, 240 nm, 245 nm and 250 nm. In agreement with the reported absorption cross section of  $\text{CCl}_3$  the two-colour signal decreases with increasing wavelength.<sup>30</sup> Mass spectra using chloroform as a precursor are given in Figure S1 in the Electronic Supplementary Information (ESI). As expected from previous work, they show  $\text{CCl}_2$  to be the dominant pyrolysis product.<sup>17, 51</sup> Typical mass spectra obtained in the femtosecond experiments using  $\text{CCl}_3\text{Br}$  with pyrolysis present (black line) and without pyrolysis (red line) are given in Figure 2. They were recorded with pump- and probe-laser present at around time zero. While the mass spectrum without pyrolysis shows no appreciable signal at all, an intense signal corresponding to  $\text{CCl}_3$  appears with active pyrolysis. Small mass peaks due to  $\text{Br}$  ( $m/z$  79/81) and  $\text{CCl}_2$  as well as  $\text{C}_2\text{Cl}_4$  ( $m/z$  164-172) are visible. Mass spectra with pump- and probe-laser only revealed a one-colour background signal that was at least a factor of ten smaller than the pump-probe signal. Note that we stopped using  $\text{CCl}_3\text{Br}$  in the ns-experiments, because the presence of several mixed

radicals  $\text{CCl}_2\text{Br}$  that were efficiently excited at shorter wavelengths complicated data interpretation.

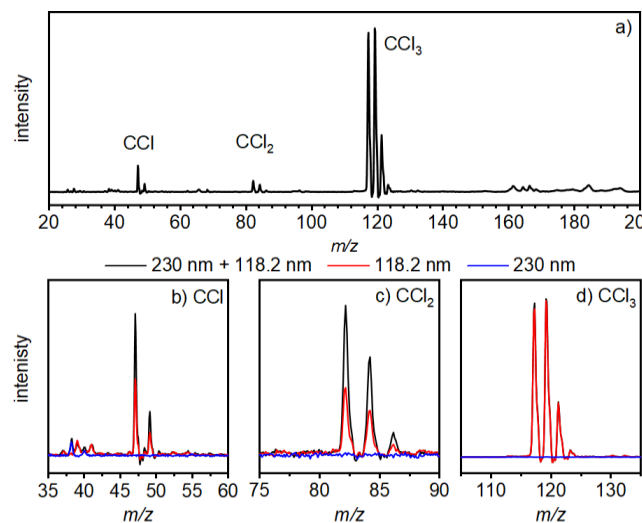


Figure 1: In a) the two-colour mass spectrum using  $\text{CCl}_4$  as a precursor recorded with 230 nm dissociation and a 118.2 nm ionisation wavelength is shown. Below, close-ups of the b)  $\text{CCl}$ , c)  $\text{CCl}_2$ , and d)  $\text{CCl}_3$  mass signals are displayed. In red the signal generated by only the ionisation laser and in blue by only the dissociation laser are shown. As visible,  $\text{CCl}$  and  $\text{CCl}_2$  signals increase in the two-colour process. For  $\text{CCl}_3$  a one-colour signal caused by the 230 nm radiation alone is present. Due to the delay between the two lasers it appears in the same region as the two-colour signals of  $m/z$  38 and 40.

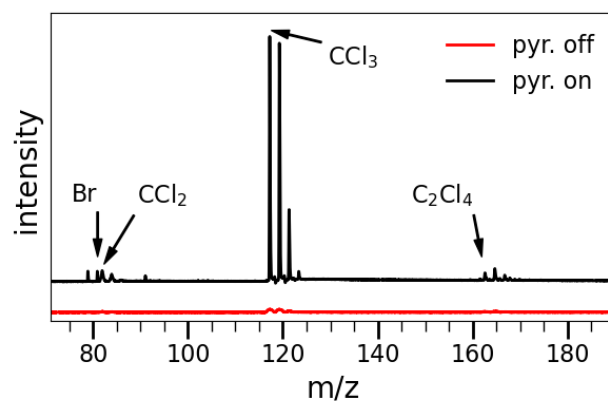


Figure 2: Mass spectra with and without pyrolysis, recorded with fs-lasers,  $\lambda_{\text{pump}} = 266$  nm and  $\lambda_{\text{probe}} = 798$  nm around time zero.  $\text{CCl}_3\text{Br}$  was employed as a precursor.

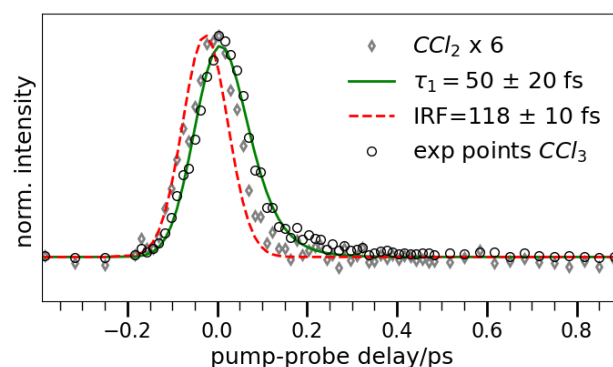


Figure 3: The time-resolved ion signal of  $\text{CCl}_3$  (open circles) at 266 nm excitation is fitted by a monoexponential decay with a time constant of 50 fs. As visible, the fit underestimates the signal intensity beyond 200 fs, indicating the presence of a second contribution. For comparison, the  $\text{CCl}_2$  signal (signal multiplied by six for ease of viewing) and the instrument response function (dashed red line) are given.

## Time-resolved experiments

To investigate the primary photophysical processes in  $\text{CCl}_3$  directly after excitation we conducted fs-time-resolved experiments, using ion and photoelectron detection. In Figure 3 the time-resolved ion signal is depicted. The  $\text{CCl}_3$  signal (open circles) decays quickly and a monoexponential fit (green line) yields a time constant of  $50 \pm 20$  fs. The instrument response function (IRF) of  $118 \pm 10$  fs employed in the fit is given as a dashed red line for comparison and shows that despite the short lifetime a reliable time constant can be extracted. At longer delay times the fit consistently underestimates the signal intensity, which indicates the presence of a second time constant on the order of 100 -150 fs. However, an accurate value cannot be determined, because the contribution to the signal is too low.

As discussed above, TR-PES provides additional information not available from the mass spectra, albeit at the cost of losing mass information. Thus, possible side products from the pyrolysis have to be considered. We therefore included the time-dependent ion signal of the most relevant side product  $\text{CCl}_2$  in Figure 3 (open diamonds). The signal was multiplied by a factor of six for a better comparison. As visible, the signal deviates only slightly from the IRF, thus the lifetime is significantly shorter than 50 fs. In addition, the signal has disappeared beyond 150 fs.

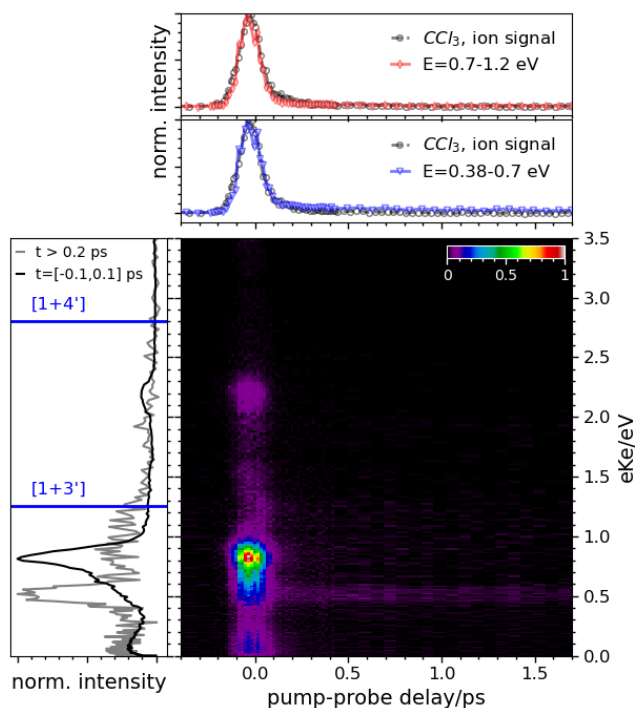


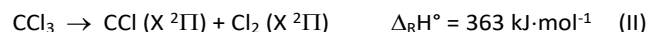
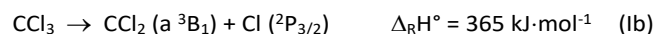
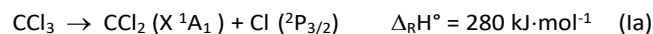
Figure 4: TR-PES spectrum with 266 nm pump/798 nm probe, displayed as a 2D-map. In the top trace the time-dependence of the photoelectron signal at two selected energy ranges is depicted and compared to the decay trace of  $\text{CCl}_3$  ion signal obtained from the mass spectra (grey open circles). The graph on the left shows the photoelectron kinetic energy summed over all delay times. The trace for  $t > 0.2$  ps has been scaled for ease of viewing. The average signal collected before the  $t_0$  was subtracted from the whole signal.

In Figure 4 the time-resolved photoelectron spectrum is displayed as 2D map. Although  $\text{CCl}_3$  dominates the mass spectrum

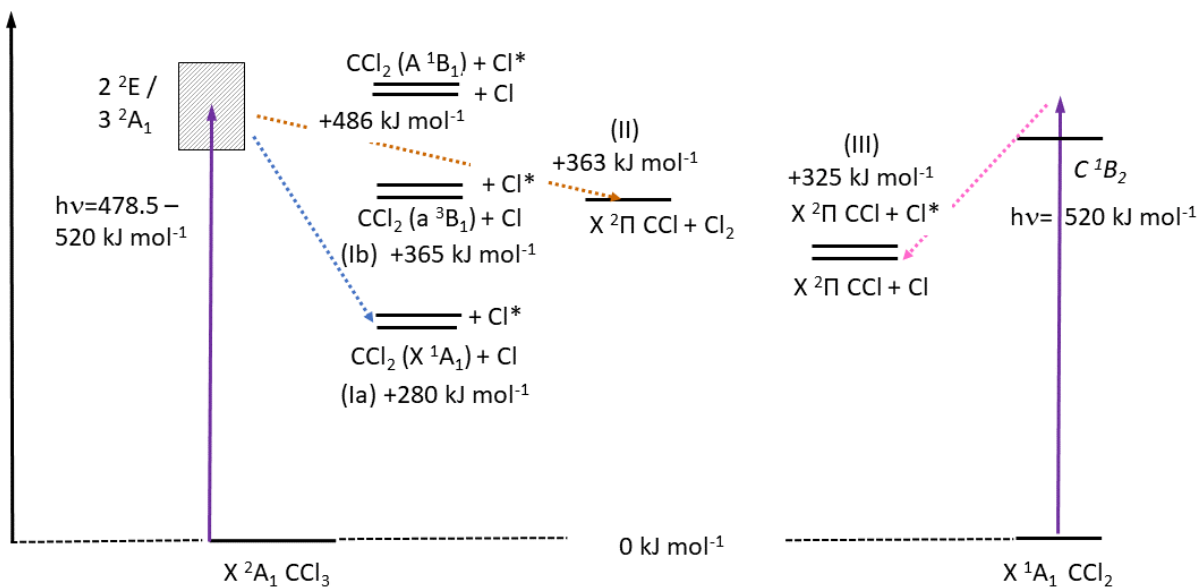
(Figure 2), small contributions from side products are present and have to be taken into account. At an electron kinetic energy (eKE) of 0.5 eV (left-hand panel) a time-dependent signal without observable decay is visible. Note that the trace for  $t > 0.2$  ps has been scaled for ease of viewing. An ion signal with the same time-dependence is observed for Br (see Figure S2), therefore we assign the signal to bromine atoms formed in the pyrolysis.<sup>#)</sup> The photoelectron signal from  $\text{CCl}_3$  itself starts at around 1 eV, trailing to lower kinetic energies. Taking the IE of 8.06 eV into account,<sup>31</sup> the eKE confirms ionisation in a  $[1+3']$  process with a total photon energy of around 9.32 eV. Two-photon excitation in the pump step can thus be excluded based on the energetics. Thus we are certain that the UV-absorption band reported by Ellermann is indeed excited, although 266 nm is close to the red edge of the band.<sup>30</sup> The shoulder to lower eKE represents transitions into vibrationally excited states of the ion that cannot be resolved due to the laser bandwidth. The vibrational envelope appears due to the large geometry change upon ionisation. A very small signal at 2.3 eV represents an  $[1+4']$  ionisation contribution. For  $\text{CCl}_2$  an IE of 9.27 eV was determined,<sup>51</sup> thus only transitions with low eKE are expected. Indeed, a peak close to 0 eV and only present around  $t_0$  can be recognized in the 2D map. We therefore assume, that the electron signal above 0.7 eV does only contain contributions from  $\text{CCl}_3$ . The time-delay traces above the 2D map show the electron signal averaged over two eKE ranges (blue and red lines). The top one (0.7-1.2 eV, red line) is indeed almost identical to the  $\text{CCl}_3$  ion signal and yields the same time constant. The lower trace, averaged over the kinetic energies from 0.38 to 0.7 eV (blue line) contains contributions from Br and is offset at late times compared to the ion signal due to the resonant ionisation of bromine atoms.

## Nanosecond Photofragment Imaging

**Photofragment imaging of  $\text{CCl}_3$  photodissociation.** In the next step, the UV photodissociation of  $\text{CCl}_3$  has been investigated between 230 nm ( $520.1 \text{ kJ}\cdot\text{mol}^{-1}/5.39 \text{ eV}$ ) and 250 nm ( $478.5 \text{ kJ}\cdot\text{mol}^{-1}/4.96 \text{ eV}$ ). In this region, two product channels are accessible, loss of a Cl atom (I) and loss of  $\text{Cl}_2$  (II). The reaction pathways are depicted in Scheme 1. Note that  $\text{CCl}_2$  can be formed in its singlet ground state or the first excited triplet state.



Both (Ia) and (Ib) can also be formed in conjunction with the spin-orbit excited  ${}^2P_{1/2}$  state of Cl ( $+0.109 \text{ eV}/10.52 \text{ kJ}\cdot\text{mol}^{-1}$ ). The first excited (open-shell) singlet state is at  $+17265 \text{ cm}^{-1}$  above the ground state ( $+206 \text{ kJ/mol}$ ) and thus barely accessible at the highest excitation energies.<sup>13</sup> It is therefore neglected in the analysis below.

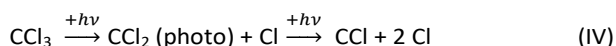


Scheme 1. Summary of the relevant dissociation pathways in  $\text{CCl}_3$  (left-hand side) and  $\text{CCl}_2$  (right-hand side). The major product of  $\text{CCl}_3$  photodissociation is dichlorocarbene in its  $X^1A_1$  ground state (blue line). Loss of  $\text{Cl}_2$  seems to be present as well (brown line).  $\text{CCl}_2$  is also formed in the pyrolysis and dissociates to  $\text{CCl} + \text{Cl}$  (magenta line).

Heats of reaction were computed from data given in the Active Thermochemical Tables (ATcT).<sup>52, 53</sup> For comparison, we computed  $\Delta_R H^\circ(0\text{K}) = 278 \text{ kJ mol}^{-1}$  for (Ia). We assume that only a negligible reverse barrier is present, so  $\Delta_R H^\circ$  is approximated to the bond dissociation energy, BDE. Formation of  $\text{CCl}$  in conjunction with two chlorine atoms is thermochemically not possible upon one-photon excitation. Nevertheless, photodissociation of  $\text{CCl}_2$  has to be considered in the analysis, because it is produced as a further pyrolysis product (see Figure 1 and Scheme 1) and dissociates after single photon absorption (III).



Alternatively,  $\text{CCl}_2$  generated in the photodissociation of  $\text{CCl}_3$  can dissociate after absorption of a second photon (IV), corresponding to two-photon dissociation of  $\text{CCl}_3$ .



Note that  $\text{CCl}_2$  (photo) generated in (Ia) or (Ib) will store part of the excess energy in the vibrational and rotational degrees of freedom, whereas  $\text{CCl}_2$  (pyro) will be cooled in the jet expansion.

The  $\text{CCl}_4$  precursor can also lose  $\text{Cl}$  or  $\text{Cl}_2$ , but the tabulated absorption cross sections at 298 K lie between 0.02 Mb at 230 nm

and  $10^{-3}$  Mb at 250 nm, two to three orders of magnitude smaller than those of  $\text{CCl}_3$ .<sup>54</sup> Indeed, we did not observe any photodissociation from pure  $\text{CCl}_4$  without pyrolysis. Nevertheless, vibrational excitation acquired in the pyrolysis might increase the photodissociation cross section. It should also be kept in mind that  $\text{CCl}_4$  is not observable in the mass spectrum and the pyrolytic conversion is thus unclear. Therefore, we will consider its thermochemistry as well.



While most experiments on  $\text{CCl}_4$  were conducted in the VUV range, Kawasaki et al investigated the photodissociation in a one-colour experiment at 235 nm ( $509 \text{ kJ} \cdot \text{mol}^{-1}$ ) and found a  $\text{Cl}/\text{Cl}^*$  ratio of 8/2, with a Boltzmann-type distribution for  $\text{Cl}$ .<sup>55</sup> However, the large translational energy release of the  $\text{Cl}^*$  atoms that extends to more than  $40 \text{ kcal} \cdot \text{mol}^{-1}$  ( $167 \text{ kJ} \cdot \text{mol}^{-1}$ ) indicates the presence of a contribution from multiphoton excitation. For (VI) a quantum yield of only 5% was found at 214 nm,<sup>56</sup> compared with >90% for (V), with its relative importance increasing towards higher excitation energies (i.e. decreasing to longer wavelengths).

In general, an image of the atomic fragment of a photodissociation, in this case  $\text{Cl}$ , is simpler and easier to interpret. However,

from the presence of Cl in (I), (III), (IV) and possibly (V) a superposition of several contributions is expected, and the additional detection of the molecular fragment is required. Therefore, in a first series of experiments, images of the  $\text{CCl}_2$  photoproduct ionized at 118.2 nm were recorded. Due to the subtraction of one-colour background signals,  $\text{CCl}_2$  generated in the pyrolysis does not contribute to the image. Formation of  $\text{CCl}_2$  from  $\text{CCl}_4$  via (VI) is neglected, due to the small quantum yield observed at 214 nm and the even lower one expected at 230 nm. Translational energy distributions  $P(E_T)$  probing  $\text{CCl}_2$  upon 230 nm (upper trace, blue) and 250 nm excitation (lower trace, red) are given

in Figure 5. The reconstructed image is visible on the right hand side. Experiments were also performed at 235 nm, 240 nm and 245 nm under the same conditions, the data are displayed in Figure S4. Note that throughout the paper we plot  $E_T$  of the respective fragment rather than the total translational energy release, because in the analysis, contributions from several molecules have to be included and compared. Excitation at 266 nm was also used for better comparison with the fs-data, but the photofragment signals beyond 250 nm were small and difficult to separate from the background signals.

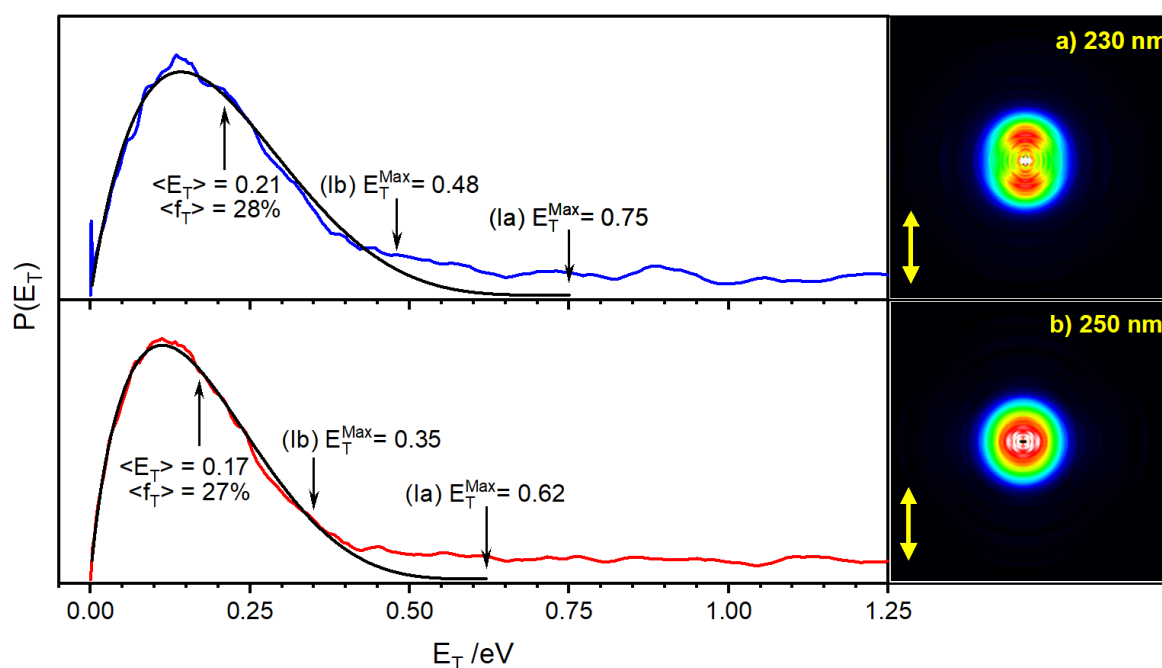


Figure 5: Translational energy distribution  $P(E_T)$  of the  $\text{CCl}_2$  fragment upon excitation with a) 230 nm and b) 250 nm light. The experimental results are drawn in blue and red respectively and a fit using expression (1) in black. The corresponding velocity map images are shown with a yellow arrow indicating the laser polarisation. Note that only the translational energy of the  $\text{CCl}_2$  fragment is plotted on the abscissa.  $\langle E_T \rangle_{\text{total}}$  amounts to 0.70 eV at 230 nm and 0.57 eV at 250 nm.

A unimodal energy distribution is observed with a shape that is independent of the dissociation wavelength. At both wavelengths, a background is visible that extends over all translational energies. The images on the right-hand side show a small anisotropy in the fragment distribution, which indicates a fast dissociation in less than a rotational period. The photofragment angular distributions (PAD) are given in Figure S6. From the PAD a value for the anisotropy parameter  $\beta$  of 0.5, is extracted at 230 nm, which decreases to around  $\beta = 0.06$  at 250 nm.

As in previous work an empirical two-parameter function was used to fit the experimental data and extract the expectation value for the translational energy release,  $\langle E_T \rangle$ .<sup>57-59</sup>

$$P(E_T) = C(E_T)^a (E_T^{max} - E_T)^b \quad (1)$$

Here  $C$  is a normalisation constant,  $a$  and  $b$  are the two fitting constants and  $E_T^{max}$  is the maximum available translational energy for the fragment upon photodissociation, computed from (2) and indicated by arrows in the Figure.

$$E_T^{max}(A) = \frac{m_B}{m_{A-B}} (\hbar\nu - BDE) \quad (2)$$

This fit is used for extracting the expectation value from the recorded data. As an example, fitting the experimental data at a dissociation wavelength of 230 nm with the two-parameter fit results in an expectation value for the fraction of excess energy released as translation,  $\langle f_T \rangle = \langle E_T \rangle / E_T^{max} = 28\%$ , assuming channel (Ia), i.e. formation of  $\text{CCl}_2$  in its electronic ground state. As visible in particular for 250 nm (lower trace),  $P(E_T)$  extends beyond the cut-off expected for formation of  $\text{CCl}_2$  in the excited triplet state, so (Ib) is considered to be of minor importance. Note that the spin-orbit splitting in Cl is  $881 \text{ cm}^{-1}$  (0.109 eV) and cannot be resolved in the data. Also product vibrations are not resolved. A summary of the values obtained at the various dissociation wavelengths is shown in Table 2.

The anisotropic photofragment angular distribution indicates a dissociation that proceeds faster than a rotational period, i.e. along a

repulsive coordinate. The expectation value of such a direct dissociation can be calculated with an impulsive model described by Tuck<sup>60</sup> and by Galloway et al.<sup>61</sup> It is based on the assumption that the available energy goes initially into the translation of Cl and C, which are considered independent from the rest of the molecule. Only after the dissociation this energy is redistributed in the molecular fragment. This simple model is appropriate for a direct dissociation, which is faster than energy redistribution in the molecule. The impulsive model yields an expectation value  $\langle f_T \rangle = 36\%$  for the total translational energy release. Considering that the geometry change in the molecular fragment during dissociation is neglected, the agreement with the experimental value is reasonable. It has been shown that impulsive (i.e. direct) C-Cl bond rupture will lead to a significant part of the excess energy ending up as  $\text{CCl}_2$  rotation.<sup>32</sup>

Table 2: Experimental values for the  $\text{CCl}_2$  fragments from  $\text{CCl}_3$  photodissociation.

$\lambda_{\text{diss}} / \text{nm}$	$E_T^{max}(\text{CCl}_2) / \text{eV}$	$\langle E_T \rangle / \text{eV}$	$\langle f_T \rangle / \%$	$\beta$
230	0.75	0.21	28	0.50
235	0.72	0.19	26	0.20
240	0.68	0.19	28	0.13
245	0.65	0.19	29	0.05
250	0.62	0.17	27	0.06

As visible in Figure 5, there is a contribution at higher translational energies that extends beyond  $E_T^{max}$  and does not originate from channel (I). It is either the result of a background signal that could not be fully subtracted, from the dissociation of one of the higher masses visible in the mass spectrum, or from a small multiphoton contribution that is present, although a low laser power was used and the beam was not focused.

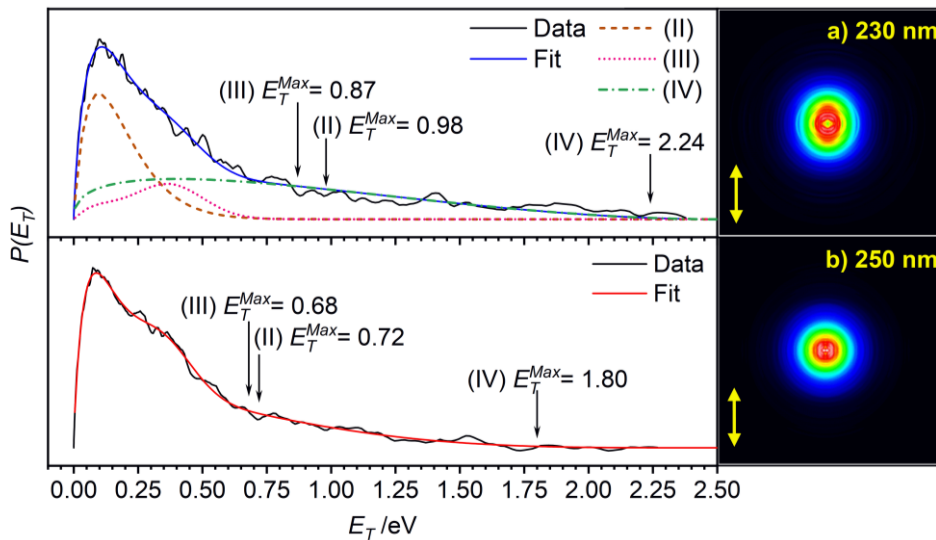


Figure 6: Translational energy distribution  $P(E_T)$  of the  $\text{CCl}$  fragment using  $\text{CCl}_4$  as a precursor. In a) 230 nm and in b) 250 nm light was used for dissociation. The experimental results are shown in black, while fits are shown in blue or red. In the upper trace the fit to the  $\text{CCl}_2$  data obtained from Figure 7 (see below) is given as a dotted magenta line, assumed contributions from  $\text{CCl}_3$  are given as a dashed brown line, while multiphoton contributions are given in green. The corresponding Velocity Map Images are shown with a yellow arrow indicating the laser polarisation. Again the translational energy of the  $\text{CCl}$  fragment is plotted on the abscissa, because  $P(E_T)$  contains contributions from the photodissociation of  $\text{CCl}_3$  and  $\text{CCl}_2$ . The red line in the bottom trace assumes similar components (scaled) at 250 nm.



The second pathway (II) for photodissociation of  $\text{CCl}_3$  leads to  $\text{CCl} + \text{Cl}_2$ , therefore velocity map images of  $\text{CCl}$  were also recorded. However, as noted above  $\text{CCl}$  can also be formed from  $\text{CCl}_2$  via (III) or (IV). Figure 6 shows  $P(E_T)$  for a) 230 nm and b) 250 nm (black curve). Data at further wavelengths are given in Figure S5. Note again that  $E_T$  of the  $\text{CCl}$  fragment is plotted on the x-axis rather than the total translational energy release, because contributions from two different molecules ( $\text{CCl}_2$  and  $\text{CCl}_3$ ) have to be considered. A bi- or multimodal distribution is evident from the shape. The contributions to the fit will be discussed below. At 250 nm excitation, the distribution maximizes around 0.1 eV, followed by a shoulder at around 0.4 eV. Furthermore, a background signal is again present, which extends to high translational energies. Anisotropy is evident at 230 nm, but less pronounced at 250 nm. Data obtained at further dissociation wavelengths are given in Figure S5. The energy cut-offs for the various product channels are indicated by arrows. As visible,  $P(E_T)$  extends beyond the limit given by reactions (II) and (III).  $E_T^{\text{max}}$  for the  $\text{CCl}$  fragment after dissociation with 230 nm light for reaction (III) is 0.87 eV, for reaction (II) 0.98 eV and for the consecutive two-photon process (IV) 2.24 eV. We thus conclude that the latter process (IV) is responsible for this contribution at large  $E_T$ . The maximum possible  $E_T$  values at the various excitation wavelengths are summarised in the ESI, Table S1.

**Photofragment imaging of  $\text{CCl}_2$  photodissociation.** To get information on the possible presence of (II) to the  $P(E_T)$  of  $\text{CCl}$ , we conducted experiments using  $\text{CHCl}_3$  as a precursor, which is known to produce predominately  $\text{CCl}_2$  upon pyrolysis (see mass spectra in Figure S1). Figure 7 shows the velocity map image of the  $\text{CCl}$  fragment after dissociation of  $\text{CCl}_2$  with 230 nm light. Two contributions are discernible, an isotropic first one at low energies (around 0.1 eV) and a second one centred at around

0.4 eV, which is strongly anisotropic. Interestingly, the high energy component visible in Figure 6 is absent, supporting its assignment to (IV). Experimental conditions (mainly pyrolysis power) were varied in order to increase and decrease the amount of  $\text{CCl}_3$  generated as a side product and additional VMIs were recorded. However, the two contributions in the  $\text{CCl}$  image did not change appreciably when the experimental conditions were changed. This confirms that both contributions belong to the dissociation of  $\text{CCl}_2$ . Its photodissociation dynamics has been investigated in detail by Dagdigian and co-workers, who monitored the  $\text{CCl}$  fragment by laser induced fluorescence,<sup>15-17</sup> and by Huber and coworkers, who employed photofragment translational spectroscopy (PTS).<sup>18</sup> The Dagdigian-group observed two different dissociation channels associated with different rotational state distributions of  $\text{CCl}$ . Thus, the two contributions obtained from the images are in qualitative agreement with this previous work. The isotropic contribution at low  $E_T$  in Figure 7 (dashed green line) is assumed to originate from a statistical process and a fit using function (1) yields  $\langle E_T \rangle = 0.15$  eV, corresponding to  $\langle f_T \rangle = 17\%$ . The high-energy contribution (dotted magenta line) is fitted by a Gaussian centred around  $\langle E_T \rangle = 0.37$  eV. Given that  $E_T^{\text{max}} = 0.87$  eV, as indicated by the arrow in Figure 7, this corresponds to  $\langle f_T \rangle = 43\%$  released into translation of the  $\text{CCl}$  fragment. Taking the translational energy of the  $\text{Cl}$  counterfragment into account, an expectation value for the total translational energy release  $\langle E_T \rangle_{\text{tot}} = 0.89$  eV (86  $\text{kJ}\cdot\text{mol}^{-1}$ ) is obtained. This process is associated with a  $\beta$ -value close to 1. Note that a more detailed study on the photodissociation dynamics of  $\text{CCl}_2$  is currently underway. PTS at 248 nm yielded a comparable value of  $\langle E_T \rangle_{\text{tot}} \approx 100$   $\text{kJ}\cdot\text{mol}^{-1}$ , corresponding to roughly 1 eV, but only a negligible anisotropy was observed.<sup>18</sup>

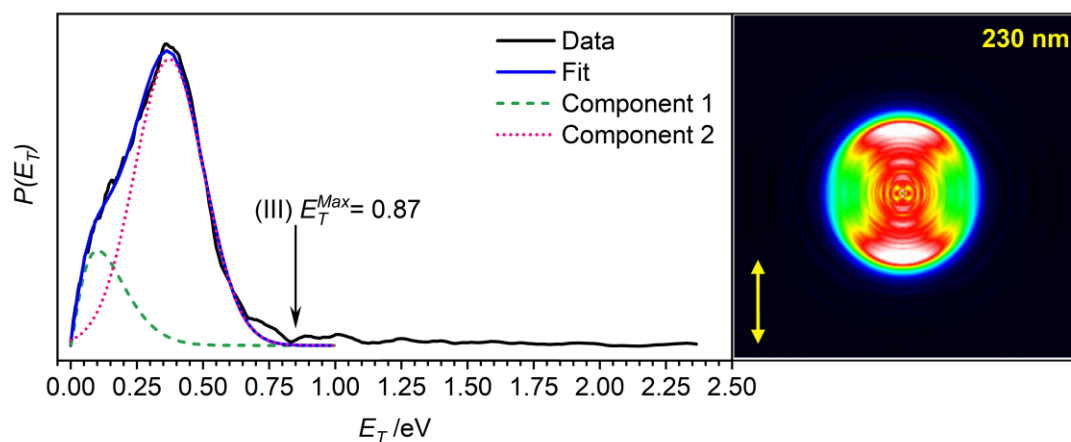


Figure 7: Translational energy distribution  $P(E_T)$  of CCl using  $\text{CHCl}_3$  as a precursor and dissociating at 230 nm. The experimental results are shown in black, while a superposition of a two-parameter fit (expression (1)) and a Gaussian distribution is shown in blue. The individual functions are drawn in dashed lines. The corresponding velocity map images are shown with an arrow indicating the laser polarisation in yellow.

Going back to the photodissociation of  $\text{CCl}_3$  in Figure 6, it is evident that the shoulder in trace b) at around 0.4 eV is due to the anisotropic component observed in reaction (III) for the photodissociation of  $\text{CCl}_2$  (dotted magenta line). However, the low energy contribution is significantly more intense in Figure 6 than in Figure 7. Concluding from the contribution at large  $E_T$ , part of the signal at all  $E_T$  will be due to (IV), indicated as a dash-dotted green line, but there seems to be an additional component that appears exclusively at low  $E_T$  (dashed brown line). It suggests that reaction (II) occurs in  $\text{CCl}_3$  as an additional contribution. The fit in the upper trace of figure 6 (full blue line) contains the various contributions. Note that due to the large number of free parameters, this fit represents only an approximation and should be considered with care. This is particularly true for the fit at 250 nm (red line), which employs a scaled  $\text{CCl}_2$  distribution. As (II) is associated with  $\text{Cl}_2$  formation, we also attempted to detect molecular chlorine via the REMPI line at 118.94 nm,<sup>62</sup> but were unsuccessful. This in turn seems to indicate that reaction (II) is of minor importance. However, it is hard to detect photofragments when the oscillator strength is distributed over a large number of transitions.

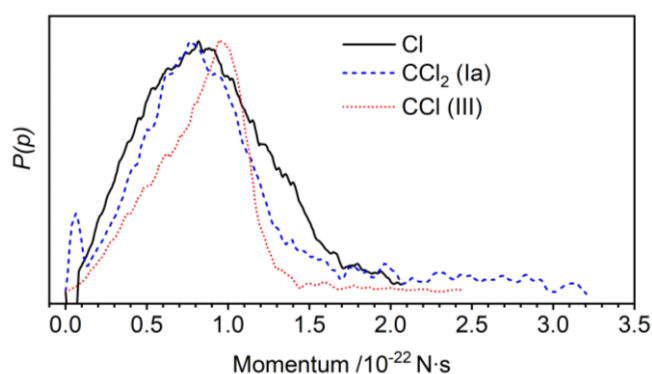


Figure 8: Translational energy distribution of atomic Cl (black) as a function of momentum, recorded at 230 nm. The blue dashed line shows the distribution expected from momentum-matching of the  $\text{CCl}_2$  signal. The red dotted line indicates the momentum matching expected for a CCl co-fragment from the photodissociation of  $\text{CCl}_2$  (III). As visible, the Cl and CCl fragments do not match well.

**Chlorine Images.** Further information on the dissociation dynamics should be available from the atomic fragment. Due to the large absorption cross section of  $\text{CCl}_3$  at 230 nm, it is not possible to monitor Cl-atoms via [2+1] REMPI at 235 nm, because the focussing conditions cause multiphoton excitation of the radical. On the other hand, a [3+1] process at 356.7 nm did not yield analysable Cl images. As in previous work, we therefore resorted to ionisation of atomic Cl in a [1+1'] process via the  $^2D_{5/2} \leftarrow ^2P_{3/2}^0$  transition, using VUV excitation at 118.9 nm.<sup>45</sup> A velocity map image of the atomic chlorine  $^2P_{3/2}$  fragment was recorded at a dissociation wavelength of 230 nm, using pyrolysis of  $\text{CCl}_4$ . It is given in Figure S7. As noted above, the spin-orbit excited  $^2P_{1/2}$  state of Cl cannot be probed by this scheme. If the Cl atom and the  $\text{CCl}_2$  fragment originate from the same process, the momenta calculated from the translational energy distributions of the two fragments should be matched with each other. The blue line in Figure 8 represents the expected Cl distribution

momentum-matched with the  $\text{CCl}_2$  distribution given in the upper trace of Figure 5, corresponding to reaction (I). As visible the maxima overlap quite well, indicating that the major part of the Cl atoms originates from process (Ia). However, the width of the distribution does not match and deviations at low and high momentum indicate that other processes contribute to the Cl-signal. Figure S8 illustrates  $P_2$  as a function of momentum for  $\text{CCl}_2$  and Cl. As visible, both follow the same trend, but for chlorine,  $P_2$  is less pronounced and even becomes negative at momenta larger  $1 \cdot 10^{-22}$  N·s. This confirms the existence of a further contribution at higher momenta that is not associated with photodissociation of  $\text{CCl}_3$ . The Cl distribution expected from reaction (III) is given as a red line in Figure 8. It should be rather narrow and centred at a slightly higher momentum, therefore it can only partially explain the deviations in the distribution. Therefore fragments produced from  $\text{CCl}_3$  after multiphoton excitation via (IV) as well as chlorine-fragments from (V) might contribute to the Cl signal over a range of translational energies or momenta, respectively.

## D Discussion

A model of the photodynamics of  $\text{CCl}_3$  can be derived by combining the information from fs time-resolved PES with the information on the dissociation products, available from photofragment imaging with ns-lasers. While the former gives insight into the processes directly after excitation, the latter sheds light on the later steps of the photochemistry. It is important to keep in mind that  $\text{CCl}_3$  is a rather complicated radical with a number of low-lying electronic states that has only scarcely been investigated. The description will therefore be less detailed than the one possible for diatomics or simple hydrocarbons.

In all experiments, the UV absorption band starting around 270 nm and previously observed by Ellerman is excited.<sup>30</sup> As evident from Table 1, the  $1^2E$ ,  $2^2E$  and the  $3^2A_1$  (3s) states lie close to each other and based on their computed oscillator strengths the latter two will contribute to this band, which has previously been assigned as  $3^2A_1$  (3s). The electron kinetic energy in the TR-PES (cf. Figure 4) shows that single photon excitation dominates and that the red edge of the absorption band is excited. The excitation energy will be rapidly redistributed between these electronic states. The time constant of around 50 fs observed in the time-resolved spectra reflects the redistribution of energy and subsequent motion out of the Franck-Condon region. Furthermore, we expect rapid depopulation of the higher excited state and transfer of the molecule to the lower-lying states, most likely  $2^2A_1$  and  $1^2A_2$ . Based on the data available for alkyl halides like  $\text{CH}_3\text{Cl}$ ,<sup>6, 63</sup> and preliminary computations, these lower lying states are expected to be repulsive with respect to the C-Cl bond. As discussed above, a second time constant is evident in the time-domain data, but cannot be accurately determined. Its presence shows that the initial 50 fs process does not correspond to the time for dissociation. We assume that it reflects this nonradiative population transfer to the

lower-lying electronic states. One has to keep in mind that fs-experiments were conducted at a single excitation wavelength only. Time constants and initial dynamics might therefore change at higher excitation energies.

At first glance it might appear appropriate to compare  $\text{CCl}_3$  with the methyl radical,  $\text{CH}_3$ . However, the latter is planar and the lowest-lying electronically excited states correspond to Rydberg-states. In contrast, the nonbonding  $p$ -orbitals on the chlorine atoms,  $n_{\text{Cl}}$  enforce a pyramidal geometry of  $\text{CCl}_3$  and additional low-energy transitions due to excitation of these orbitals. Thus nonradiative deactivation pathways are available that are not present in methyl.

While TR-PES unravels the early steps of the dynamics, photo-fragment imaging gives information on the product state distributions, i.e. the processes that occur after the rapid population transfer to the lower-lying states. The ns-data show that reaction (I) dominates, i.e. loss of Cl, associated with  $\text{CCl}_2$ . As visible in Scheme 1, four pathways are possible for loss of a chlorine atom, leading to  $\text{CCl}_2$  either in the  $X^1A_1$  ground state or the  $a^3B_1$  excited triplet state. Both can be formed with a Cl atom in the  $^2P_{3/2}$  ground state or the  $^2P_{1/2}$  spin-orbit excited state, which are separated by  $10.52 \text{ kJ}\cdot\text{mol}^{-1}$ . The latter two cannot be distinguished in the translational energy distribution. Due to side reactions contributing to the Cl signal, most information on (I) is available when the  $\text{CCl}_2$  molecular fragment is monitored.

Interpretation of the data and derivation of a dissociation model are not straightforward. The image shows a unimodal distribution, with the fraction of excess energy released into product translation  $\langle f_T \rangle = 26\text{-}29\%$ , assuming formation of  $\text{CCl}_2$  in the  $X^1A_1$  ground state (Ia). Formation of  $\text{CCl}_2$  in the  $a^3B_1$  state (Ib) would also be thermochemically possible, but  $P(E_T)$  extends beyond the maximum translational energy expected for this reaction, so the  $X^1A_1$  product state has to dominate. For example, at 250 nm, the observed  $\langle E_T \rangle$  would correspond to  $\langle f_T \rangle \approx 60\%$  assuming a triplet product, far above the range expected for statistical as well as impulsive dissociation. In addition,  $P(E_T)$  is unimodal and  $\beta$  does not vary with translational energy. Due to the radical temperature in the jet of 150 K (vide supra) hot band transitions might contribute, but especially at 250 nm excitation they cannot explain the shape of  $P(E_T)$  when compared with previous work.<sup>43, 64</sup> Therefore, we assume that (Ia) dominates and contributions from (Ib) are small, if present at all. Formation of  $\text{CCl}_2$  ( $A^1B_1$ ) is energetically possible at the highest excitation energies, but not consistent with the observed  $P(E_T)$ . As the molecular fragment is monitored and the VUV detection scheme cannot probe  $\text{Cl}^*$ , there is no information on the spin-orbit branching ratio. The shape of  $P(E_T)$  appears Boltzmann-like and at first glance seems to indicate a ground state dissociation after redistribution of vibrational energy, following a statistical mechanism. However, 26-29% of the excess energy are released into translation, which is significantly more than usually observed in a statistical distribution. In the statistical photodissociation of cyclic hydrocarbons<sup>64, 65</sup> and aryl chlorides at 193 nm<sup>66</sup> values for  $\langle f_T \rangle$  between 10% and 12% have been observed, while in the H-atom loss from hydrocarbon

radicals  $\langle f_T \rangle$  of up to 15 to 20% have been reported.<sup>67, 68</sup> Thus in the present work  $\langle f_T \rangle$  exceeds the range of values previously observed for statistical dissociation. In addition, an anisotropic PAD with a positive  $\beta$  is observed, which suggests that dissociation is faster than a rotational period and thus supports a model based on a direct dissociation. According to preliminary computations, both the  $2^2A_1$  and  $1^2A_2$  states of  $\text{CCl}_3$  result in a dissociation to the  $X^1A_1$  state of  $\text{CCl}_2$ . Dissociation in these states would be commensurate with the observations. From an impulsive model for dissociation along a repulsive coordinate we expect a larger  $\langle f_T \rangle = 0.36$ , but this simple approach neglects effects like geometry changes during the dissociation and should thus be seen as a limiting case. Interestingly,  $\beta$  decreases with an increase in wavelength from 0.5 at 230 nm to 0.06 at 250 nm (see Figure S6), suggesting either a slower dissociation at lower energies or an involvement of different electronic states. Different contributions of the  $2^2E$  ( $D_4$ ) and  $3^2A_1$  ( $D_5$ ) states to the initial absorption might lead to different anisotropies. As for the  $2^2E$  state  $\mu_T$  is oriented in the C-Cl plane, we expect a positive  $\beta$ -value for the Cl photofragment angular distribution, whereas for the (most likely planar)  $3^2A_1$  state, a negative  $\beta$  is expected, because  $\mu_T$  is oriented along the symmetry axis.<sup>69</sup> Therefore, the contribution of the  $2^2E$  state to the absorption band might increase to the blue and possibly lead to a change of dissociation mechanism with excitation energy. However, the almost constant shape of  $P(E_T)$  at all wavelengths does not support this model. We therefore suggest an alternative explanation, a stepwise deactivation of the optically excited state. At lower excitation energies,  $\text{CCl}_3$  could be trapped for a few vibrational periods in an intermediate state (e.g. the  $1^2A_2$ ), sufficiently long to partially lose its anisotropy, whereas at higher excitation energies such a barrier is rapidly surmounted. Note that the rise time of the two-colour signal (Figure S3) is on the scale of the laser pulse duration, in agreement with a dissociation on a sub-ns time scale. High-level computations are required to verify this model.

The only previous study on  $\text{CCl}_3$  photodissociation was reported by Hintsä et al, who excited the radical at 308 nm and observed the  $\text{CCl}_2$  fragment by translational energy spectroscopy.<sup>32</sup> Here,  $\text{CCl}_3$  was generated by photolysis of  $\text{CCl}_4$  at 193 nm, so radicals were most likely internally hot. Hintsä et al observed a total translational energy release of less than 30% and  $\beta = 1.0 \pm 0.2$ , in qualitative agreement with the present results. No indication of pathway (II), loss of  $\text{Cl}_2$  was found in this work.

Besides the  $\text{CCl}_2$  molecular fragment, the Cl signal has also been analysed at 230 nm. Momentum matching of  $\text{CCl}_2$  and Cl fragments and a comparable anisotropy parameter  $\beta$  indicate that both fragments predominately originate from the same source. However, there are visible differences that suggest contributions from competing processes to the Cl signal, possibly dissociation of  $\text{CCl}_2$  (III) or  $\text{CCl}_4$  (V) as well as multiphoton-processes (IV), so it is difficult to disentangle their contribution from (I).

In addition to Cl-loss, pathway (II) to  $\text{CCl} + \text{Cl}_2$  is also thermochemically accessible (see Scheme 1). The CCl images show two distinguishable features, a dominant low energy one, which

maximizes at around 0.1 eV and a second one centred around 0.4 eV. However,  $\text{CCl}_2$ , which is a minor product in the pyrolysis can also dissociate to  $\text{CCl}$  (see right-hand side of Scheme 1). Control experiments using  $\text{CHCl}_3$ , a known precursor for  $\text{CCl}_2$ , also yield a bimodal translational energy distribution for the  $\text{CCl}$  photofragment. The higher energy component, centred at 0.4 eV is dominant in the experiments utilizing  $\text{CHCl}_3$  and can thus be assigned to pathway (III), photodissociation of  $\text{CCl}_2$  produced in the pyrolysis to  $\text{CCl} + \text{Cl}$ . The anisotropic PAD for this main peak with  $\beta$  between 0.7 and 1 and the large  $\langle f_T \rangle$  of about 43% indicate that  $\text{CCl}_2$  dissociates to  $\text{CCl}$  along a repulsive coordinate. An impulsive model yields  $\langle f_T \rangle = 0.41$ , in almost perfect agreement with the experiment. The origin of a low energy contribution in the photodissociation of  $\text{CCl}_2$  is still being investigated, but the smaller  $\langle f_T \rangle$  and the absence of anisotropy point towards a statistical mechanism. With this information, the peaks in the  $\text{CCl}$  image from  $\text{CCl}_4$  as a precursor can be assigned. The distribution derived from the  $\text{CCl}_2$  experiment is given as a dotted magenta line in the upper trace of Figure 6 (230 nm dissociation). The shoulder at around 0.4 eV is attributed to the direct dissociation of  $\text{CCl}_2$  formed in the pyrolysis and not related to  $\text{CCl}_3$  photodissociation. However, the low energy contribution at around 0.1 eV is significantly larger than in the  $\text{CCl}_2$  experiments, thus it seems to originate partially from  $\text{CCl}_3$  dissociation. This additional contribution at low energy is depicted as a dashed brown line in the figure. The  $P(E_T)$  of  $\text{CCl}$  also shows a signal that extends to high translational energies and requires absorption of two photons. This component must originate from the consecutive process (IV), which deposits extra internal energy in the  $\text{CCl}_2$  and thus leads to a broad  $P(E_T)$ . It is indicated as a dash-dotted green line in the Figure. It is difficult to imagine that the strong component maximizing at  $E_T = 0.1$  eV is exclusively due to this sequential process. Thus we conclude that reaction (II) contributes to this component, represented as a dashed brown line in Figure 6. We point out that the counter-fragment  $\text{Cl}_2$  has not been detected. Quantification of the various reaction channels is not possible, because the ionisation cross sections  $\sigma_{\text{ion}}$  of  $\text{CCl}_2$  and  $\text{CCl}$  are not known. Compared to alkyl chlorides, one important difference should be noted. In many alkyl halides, the spin orbit branching ratio of chlorine is determined by the interaction between the  $^3\text{Q}_0$  and the  $^1\text{Q}$  states. In  $\text{CCl}_3$ , however, all low-lying excited states are doublets, with the quartet states higher in energy. Direct dissociation of a quartet state corresponds to a  $\text{CCl}_2$  fragment either in the triplet (Ib) or the open-shell singlet state. The present work provides no evidence for either product and thus rules out dissociation from a quartet state. Nevertheless, quartet states might be involved in the non-radiative relaxation. The question of whether such interactions lead to the formation of spin-orbit excited chlorine atoms remains open.

## Conclusions

The photodissociation dynamics of  $\text{CCl}_3$  upon UV excitation was investigated by fs time-resolved photoionisation and photofragment imaging of the reaction products to follow the photodynamics along the complete reaction coordinate. The radical was

generated by pyrolysis of  $\text{CCl}_4$  and  $\text{CH}_3\text{Br}$ . Excitation between 230 nm and 266 nm is due to transitions into the  $\text{D}_4$  ( $^2\text{E}$ ) and  $\text{D}_5$  ( $^2\text{A}_1$ ) states, as indicated by TD-DFT. The fs-experiments show a rapid motion out of the Franck-Condon window within around 50 fs. A second slightly longer time constant is recognisable, but cannot be determined accurately. It is most likely due to a fast nonradiative deactivation to lower-lying dissociative electronic states. Here, the fate of the radicals was monitored by photofragment imaging. Dissociation of  $\text{CCl}_3$  leads to  $\text{CCl}_2 + \text{Cl}$ . A velocity map image of the  $\text{CCl}_2$  photofragment shows an anisotropic distribution and a translational energy release of 26-29%, indicating a dissociation in less than a rotational period. The  $\text{Cl}$ -fragment image is to a large extent momentum matched and the  $\beta$ -parameter is similar, but it contains additional contributions, in part from the photodissociation of  $\text{CCl}_2$ , which is produced in the pyrolysis in small amounts. Furthermore, as the photoproduct from  $\text{CCl}_3$  it can absorb a second photon and dissociate.

Images of  $\text{CCl}$  were recorded to get insight into the second reaction pathway, leading to  $\text{CCl} + \text{Cl}_2$ . Control experiments using the pyrolysis of  $\text{CH}_3\text{Cl}$ , a known  $\text{CCl}_2$  precursor, revealed the contribution of  $\text{CCl}_2$  dissociation to the  $\text{CCl}$  fragment signal. An anisotropic component centred at around 0.4 eV is due to direct dissociation of  $\text{CCl}_2$ . An isotropic one at low translational energies increases significantly when  $\text{CCl}_3$  is present, indicating the presence of reaction (II), dissociation of  $\text{CCl}_3$  to  $\text{CCl} + \text{Cl}_2$ . The long tail in the translational energy distribution shows the presence of a multiphoton process, i.e. stepwise dissociation of  $\text{CCl}_3$ , thus the  $\text{CCl}$  contribution that originates from (II) cannot be quantified.

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## Notes and references

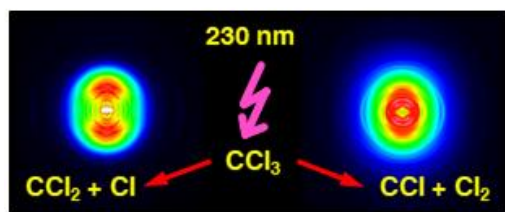
‡ Bromine has an IE of 11.81 eV. Ionisation via a [1+5'] or [2+2'] process with a total energy of 12.41 eV would be in agreement with  $e\text{KE} \approx 0.5$  eV, assuming a non-perfect energy calibration. However, an alternative origin might be the dissociative photoionisation of  $\text{Br}_2$  formed in the pyrolysis reactor in a [1+4'] process,  $\text{AE}(\text{Br}^+, \text{B}_2) = 10.48$  eV.

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TOC Figure:



The photodissociation dynamics of  $\text{CCl}_3$  has been investigated by femtosecond photoelectron and nanosecond photofragment spectroscopy, using velocity map imaging.