PHOTODISSOCIATION DYNAMICS OF HALOGENATED THIOPHENES AT 235 nm:
A REMPI TOF STUDY

7.1 INTRODUCTION

Recently, many experiments in the ultraviolet (UV) region, accompanied by theoretical studies have been performed, to investigate the photodissociation dynamics of organic halogenated molecules having C–X (X = Cl, Br, and I) bonds. The most of such type of studies have focused particularly on the mechanism of the formation of X atom in its ground, X ($^2\text{P}_{3/2}$), and spin-orbit excited, X*($^2\text{P}_{1/2}$), states. However, such studies for more complex molecules, especially, cyclic compounds, have been less keenly pursued because of their complex photodissociation mechanism, which also include multiple channels. In this context a detailed study was undertaken, to understand the dynamics of X/X* formation in the photodissociation of halogen-containing thiophenes.

Thiophene (c-C$_4$H$_4$S) is a five-membered heterocyclic compound, containing four carbon atoms and one sulfur atom in the ring. The delocalization of electron lone pairs on sulfur, in the conjugated $\pi$ system, makes thiophene behave like an aromatic
compound. This electron delocalization makes thiophene and thiophene-based materials and polymers an important building block entity for manufacturing various materials, showing unusual electronic and optical properties. The photochemistry of thiophene, especially in the UV region, has been a subject of many investigations, both experimentally and theoretically. To cite a few, the experimental work includes the studies related to its UV absorption spectrum in the gas phase and the electron energy loss spectrum. A few experiments were also done, to understand its excited-state dynamics, using femtosecond pump-probe photoelectron spectroscopy and resonance Raman spectroscopy. On the theoretical side, the studies include the electronic structure calculations in the Franck-Condon region, with complete active space self-consistent field and density functional theory. Similarly, ab initio multi-reference configuration interaction calculations were performed to understand its UV spectrum. A few other studies were also carried out to investigate its ultrafast internal conversion, and photodissociation dynamics. Very recently, ultrafast deactivation processes of thiophene were studied theoretically by Cui and Fang, and Stenrup.

The gas phase UV absorption spectrum of thiophene shows an A-band located at 225 nm (5.5 eV), in the lowest valence state, which has a long vibrational progression, with the lowest absorption at ~240 nm (5.15 eV). This has been attributed to the vibrational origin of the $1^1A_1 \rightarrow 2^1A_1$ or simply a $\pi \rightarrow \pi^*$ transition. Wiebe and Heicklen studied the UV photochemistry of thiophene at 213.9, 228.8, and 253.7 nm, in the gas phase, using end-product analysis. Nayak et al. proposed a mechanism for infrared multiphoton dissociation (IRMPD) that involves breakage of the C–S bond in thiophene, to form an unstable 1,5-diradical, which further decomposes via different channels. Flash photolysis of thiophene showed a transient
absorption spectrum in the region 377-417 nm\textsuperscript{187}, which was tentatively assigned to the absorption due to the transient C\textsubscript{4}H\textsubscript{3} radical. Ng and coworkers\textsuperscript{188} studied photodissociation of thiophene at 193 nm using photoionization detection of the hydrocarbon products and (2+1) REMPI detection of the sulfur atom. They observed only two dissociative channels, namely, C\textsubscript{2}H\textsubscript{2}S + C\textsubscript{2}H\textsubscript{2} and C\textsubscript{4}H\textsubscript{4} + S. Later on, similar studies were done at 193 nm by Suits and co-workers\textsuperscript{189}, using synchrotron radiation as a universal product probe. They observed five primary channels and concluded that all the dissociation processes occur on the ground-state surface, following fast internal conversion.

Among the various substituted thiophenes, the halogen-substituted thiophenes are the most studied thiophenes from the viewpoint of photochemistry and applications thereof. The photoelectron studies on 2-bromothiophene\textsuperscript{190} and 2-chlorothiophene\textsuperscript{191} suggest that the lone pair electrons on Br and Cl atoms exist in two different orbitals. The orbital lying in the molecular plane does not mix with the ring orbitals, to a significant extent, whereas the other one, which is perpendicular to molecular plane, is delocalized over much of the ring, and significantly involved in bonding and mixing with π electrons of the ring. In the case of 2-bromothiophene, the molecular orbital associated with the in-plane lone pair on bromine atom retains its atomic character, to a great extent than the molecular orbital corresponding to the out-of-plane component. However, in the case of chlorine, the chlorine atomic character is of minor importance. In the UV spectrum of dihalogenated thiophene\textsuperscript{175} in solution phase, two π*←π electronic transitions were observed. Also, in the stretched sheet polarized spectrum of 2,5-dibromothiophene\textsuperscript{192}, two bands were observed, which were polarized. Very recently, positive and negative photoion spectroscopy studies on monochlorothiophenes were conducted, using synchrotron vacuum ultraviolet
Photodissociation dynamics of halogenated thiophenes at 235 nm

Wang and co-workers\textsuperscript{194} studied the dynamics of Br atom formation in the photodissociation of bromothiophenes at 267 nm, using ion velocity imaging technique. The presence of another chromophore, namely the C–X bond, can alter the photochemistry. Competitive absorption may exist between these two chromophores, when the molecules absorb photons at a particular wavelength.

In this context, the present study is undertaken to understand the photodissociation dynamics of two halogen substituted thiophenes, namely, 2-chlorothiophene and 2-bromo-5-chlorothiophene. Here, we have investigated dynamics of halogen atom (X/X*) formation, around 235 nm, in a supersonic molecular beam, using the REMPI-TOF technique. We have also measured the translational energy distributions for both the types of chlorine and bromine atoms. Besides, we have also measured the relative quantum yields of Cl* and Br*. To gain further insights, the anisotropy parameters ($\beta$) are also measured. Further, theoretical calculations have been carried out to understand the dissociation dynamics.

7.2 EXPERIMENTAL SECTION

Studies on photodissociation dynamics of 2-chlorothiophene and 2-bromo-5-chlorothiophene have been carried out in a molecular beam, using REMPI, with time-of-flight (TOF) mass spectrometry, to monitor the chlorine and bromine photoproducts state selectively. The experimental set-up has been discussed in detail in Chapter 2, Section 2.3.1. The halogenated thiophenes samples, 2-chlorothiophene (96% purity, Aldrich) and 2-bromo-5-chlorothiophene (98% purity, Aldrich), were used without further purification. The chlorine and bromine atoms were probed, using (2+1) REMPI transitions in the 234-236 nm region. A typical REMPI scheme for the chlorine atom and for the bromine atom is shown in Chapter 2, FIG. 2.6 and FIG. 2.7, respectively. The two lines for chlorine atom were selected from several lines, shown
in Table 6.1 and FIG. 6.2 of Chapter 6 for quantitative measurements. The bromine atom was probed by (2+1) REMPI transitions in the region of 234-236 nm, shown in FIG. 7.1. The two REMPI lines were chosen from various lines, shown in Table 7.1, and the REMPI spectra are compared with the literature values. The peaks at 233.70 nm (42789.9 cm\(^{-1}\), 6p \(^4\)P\(_{3/2}\)\(\leftarrow\)4p \(^2\)P\(_{3/2}\)) and 234.04 nm (42727.7 cm\(^{-1}\), 6p \(^2\)S\(_{1/2}\) \(\leftarrow\) 4p \(^2\)P\(_{1/2}\)) were probed for the present experiment.

**FIG. 7.1:** Various REMPI lines for bromine atom formed during the photolysis of bromoform.
Table 7.1. Comparison of experimental and literature REMPI lines for Br.

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Experimental wavelength (cm⁻¹)</th>
<th>Experimental wavelength nm</th>
<th>Literature wavelength (cm⁻¹)</th>
<th>Literature wavelength nm</th>
<th>Two photon Transition From 4p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42782.5</td>
<td>233.74</td>
<td>42789.9</td>
<td>233.70</td>
<td>6p⁻¹P₃/2 ← 4p⁻²P₃/2</td>
</tr>
<tr>
<td>2</td>
<td>42718.6</td>
<td>234.09</td>
<td>42727.7</td>
<td>234.04</td>
<td>6p⁻²S₁/2 ← 4p⁻²S₁/2</td>
</tr>
<tr>
<td>3</td>
<td>42660.2</td>
<td>234.41</td>
<td>42671.2</td>
<td>234.35</td>
<td>6p⁻²D₅/2 ← 4p⁻²P₁/2</td>
</tr>
<tr>
<td>4</td>
<td>42623.9</td>
<td>234.61</td>
<td>42631.1</td>
<td>234.57</td>
<td>6p⁻⁴S₃/2 ← 4p⁻²P₁/2</td>
</tr>
<tr>
<td>5</td>
<td>42567.6</td>
<td>234.92</td>
<td>42578.5</td>
<td>234.86</td>
<td>6p⁻²D₃/2 ← 4p⁻²P₁/2</td>
</tr>
<tr>
<td>6</td>
<td>42498.9</td>
<td>235.30</td>
<td>42495.3</td>
<td>235.32</td>
<td>5p⁻²F₅/2 ← 4p⁻²P₁/2</td>
</tr>
<tr>
<td>7</td>
<td>42385.4</td>
<td>235.93</td>
<td>42434.0</td>
<td>235.66</td>
<td>5p⁻²P₁/2 ← 4p⁻²P₁/2</td>
</tr>
<tr>
<td>8</td>
<td>42372.8</td>
<td>236.00</td>
<td>42396.2</td>
<td>235.87</td>
<td>5p⁻²P₃/2 ← 4p⁻²P₁/2</td>
</tr>
</tbody>
</table>

The power dependence studies of one-colour REMPI intensities for transitions corresponding to Cl (²P₃/2), produced on photolysis of 2-chlorothiophene at ~235 nm, show linear behaviour in the log-log plot with a slope of ~2.9±0.1. This observation is consistent with one-photon dissociation of 2-chlorothiophene, followed by (2+1) REMPI of chlorine. Similar power dependence studies were carried out for one colour REMPI transitions, corresponding to Cl (²P₃/2) and Br (²P₃/2), produced on photolysis of 2-bromo-5-chlorothiophene. The FIG. 7.2 shows linear behaviour in the log-log plot of REMPI signal against laser intensity for Br (²P₃/2), with a slope of 3.3±0.2. Apart from the power dependence studies, we also systematically monitored the shape and the width of TOF profiles of Cl and Br atoms at various laser intensities. The TOF profiles remain invariant at lower laser intensities in the range of 50-75 μJ/pulse. However, for TOF profiles, the energy used was even lower as compared to above mentioned energy. All the experiments were performed at much lower intensity (typically at ~ 300 μJ/pulse) than that at which the shape and the width of the TOF
profiles start varying. This experimental condition ensures that the translational energy distributions and the anisotropy parameters are invariant over the laser fluences used.

FIG. 7.2: Dependence of the REMPI signal of Br($^3P_{3/2}$) atom from 2-bromo-5-chlorothiophene photolysis on the laser intensity. The slope of the fitted linear log-log plot is 3.3±0.2.

The translational energy distribution ($E_T$) and the anisotropy parameter ($\beta$) for Cl, Cl*, Br and Br* were determined by measuring their TOF profiles at different laser polarizations, using a commonly used forward convolution (FC) technique, as described in Chapter 2, Section 2.3.2. In this method, the knowledge of the instrumental response function is required, and the same was determined by studying the REMPI of aniline$^{195}$ beam. These measurements showed the instrumental response function to be well described by a Gaussian function in the time domain, with FWHM of 27 ns at aniline mass. Under space focusing conditions, this leads to a
convolution function in the velocity domain, which is linearly dependent on the extractor voltage $V_{\text{ex}}$.

In the present work, we have used a procedure of non-core sampling data, in which it is assumed that the nature and the shape of the TOF profiles for chlorine/bromine photofragment is independent of the probe polarization. In general, this assumption holds good. However, the presence of atomic $v \cdot j$ correlation may make this assumption only approximate. However, these correlations are weak enough to be neglected.

7.3 RESULT AND ANALYSIS

7.3.1 SPIN-ORBIT BRANCHING RATIO

The relative quantum yields of the halogen atom (X) fragments, formed in different spin-orbit states (X, X*), were evaluated for both the compounds studied. The relative yields were calculated by normalizing the integrated intensity, i.e., the peak areas $S(X)$, or $S(X^*)$, of the respective (2+1) REMPI transitions with respect to the laser intensity, and the ratio of the two-photon absorption coefficients. As discussed earlier, the REMPI spectra of the ground X($^2P_{3/2}$) and the spin-orbit excited X*($^2P_{1/2}$) atomic photoproducts were scanned around 42492.5 and 42516.1 cm$^{-1}$ respectively, for the chlorine atom, and around 42789.9 and 42727.7 cm$^{-1}$ respectively, for the bromine atom. The ratio of the measured areas $S(X)$ and $S(X^*)$ of (2+1) REMPI lines is proportional to the product ratio, $N(X)/N(X^*)$, as given in equation (7.1),

$$\frac{N(X^*)}{N(X)} = k \frac{S(X^*)}{S(X)}$$

(7.1)

where k is the relative ionization probability. The intensities $S(X)$ and $S(X^*)$ were obtained by integrating the measured ion signal intensities over the proper range, covering the Doppler width and the probe laser bandwidth. The measurements were
Repeated at different laser light intensities, which gave similar relative signal intensities. For photodissociation of 2-chlorothiophene, the integrated ion signal intensity ratio, $S(\text{Cl}^*)/S(\text{Cl})$, was measured to be $0.23\pm0.07$ (FIG. 7.3). Similarly, for 2-bromo-5-chlorothiophene, the integrated ion signal intensity ratios, $S(\text{Cl}^*)/S(\text{Cl})$ and $S(\text{Br}^*)/S(\text{Br})$, were measured to be $0.23\pm0.07$ (FIG. 7.4[a]) and $0.09\pm0.03$ (FIG. 7.4[b]), respectively. From the measured integrated intensity ratios, one can easily obtain the product ratios, using equation (7.1), in which the relative ionization probability, $k$ was taken to be $0.85\pm0.10$ for chlorine atom$^{197}$ and $0.17\pm0.05$ for bromine atom$^{198}$. The $\Phi(X^*)$ can be obtained from an expression

$$\Phi(X^*) = \frac{N(X^*)}{N(X^*)+N(X)} \quad (7.2)$$

![FIG.7.3: REMPI spectral profiles of Cl and Cl* atoms produced in photodissociation of 2-chlorothiophene at 235 nm, used for the determination of their relative quantum yields.](image-url)

The $\Phi(\text{Cl}^*)$ obtained in the photodissociation of 2-chlorothiophene is found to be $0.19\pm0.06$. Similarly, the $\Phi(\text{Cl}^*)$ and $\Phi(\text{Br}^*)$ in the photodissociation of 2-bromo-5-chlorothiophene are found to be $0.19\pm0.06$ and $0.08\pm0.03$, respectively.
TRANSLATIONAL ENERGY DISTRIBUTION AND ANISOTROPY PARAMETER

The TOF profiles of the Cl, Cl*, Br and Br* atoms were converted to the velocity domain for both the halogenated thiophenes, as discussed in the Section 2.3.2, Chapter 2. Their TOF profiles have been found to be independent of laser polarization, for both the compounds studied. In FIG. 7.5 we have shown two panels corresponding to the typical TOF profiles recorded for the Cl/Cl*, or Br/Br*, fragments, for the laser polarization at the magic angle ~54.7° to the detection axis.

FIG. 7.4: REMPI spectral profiles produced in photodissociation of 2-bromo-5-chlorothiophene at 235 nm; (A) Cl and Cl* and (B) Br and Br*, used for the determination of their ratio.

7.3.2 TRANSLATIONAL ENERGY DISTRIBUTION AND ANISOTROPY PARAMETER

The TOF profiles of the Cl, Cl*, Br and Br* atoms were converted to the velocity domain for both the halogenated thiophenes, as discussed in the Section 2.3.2, Chapter 2. Their TOF profiles have been found to be independent of laser polarization, for both the compounds studied. In FIG. 7.5 we have shown two panels corresponding to the typical TOF profiles recorded for the Cl/Cl*, or Br/Br*, fragments, for the laser polarization at the magic angle ~54.7° to the detection axis.
FIG. 7.5: REMPI-TOF profiles; (A) Cl ($^2P_{3/2}$) and Cl* ($^2P_{1/2}$) produced from the photodissociation of 2-chlorothiophene; (B) Cl ($^2P_{3/2}$) and Cl* ($^2P_{1/2}$) and (C) Br ($^2P_{3/2}$) and Br* ($^2P_{1/2}$) produced from the photodissociation of 2-bromo-5-chlorothiophene at 235 nm. The circles are the experimental data and the solid curves are forward convolution fit. Velocity components are depicted as dotted curves. The profiles correspond to the magic angle ($\chi=54.7^\circ$) experimental geometry.

We analyzed the TOF data, using a forward convolution procedure, as described in the Section 2.3.2, Chapter 2. The predicted TOF spectra were calculated, convoluted with the instrumental response function, and compared with the experimental results. The solid curves in FIG. 7.5 display the final calculated TOF profiles. However, we get two components in the profiles of Cl atom produced in photodissociation of 2-chlorothiophene (shown in FIG. 7.5[A]), each component is shown by the dot-dash curves, and the sum by the solid line. The photofragment translational energy distributions, $P(E_T)$, determined from the data in the FIG. 7.5, for the Cl/Cl* and Br/Br*, are depicted in FIG. 7.6 for 2-chlorothiophene and 2-bromo-5-chlorothiophene. Inspection of $P(E_T)$ figures reveals that the translational energy distribution, $P(E_T)$, has two components for Cl atom and only one component for Cl* produced in photodissociation of 2-chlorothiophene. However, both Cl and Br atoms...
produced in the case of 2-bromo-5-chlorothiophene have only one component. In the case of 2-chlorothiophene, the average translational energies for the fast and the slow components of the Cl channel are 3.0±1.0 and 1.0±0.5 kcal/mol, respectively. The faster component constitutes of 80±5% of the total fragments, while the slower component constitutes of the remaining 20±5%. For Cl*, which has only one component, the average translational energy is 3.5±1.0 kcal/mol. In the case of 2-bromo-5-chlorothiophene, as mentioned, we have observed only one component for Cl, Cl*, Br and Br* in the translational energy distribution. The average translational energies of the Cl and Cl* channels are 3.5±1.0 and 5.0±1.0 kcal/mol, respectively. Similarly, the average translational energies of the Br and Br* channels are 2.0±1.0 and 3.5±1.0 kcal/mol, respectively. Since the TOF profiles for Cl/Cl* and Br/Br* are independent of laser polarizations, the β parameter is well characterized by a value of 0.0, within the experimental uncertainties.
FIG. 7.6: Centre-of-mass recoil translational energy distribution derived from FIG. 7.5: (A) Cl($^2P_{3/2}$) and Cl* ($^2P_{1/2}$), produced in the photodissociation of 2-chlorothiophene, (B) and (C) Cl($^2P_{3/2}$) and Cl* ($^2P_{1/2}$) and Br ($^2P_{3/2}$) and Br* ($^2P_{1/2}$), produced in the photodissociation of 2-bromo-5-chlorothiophene, respectively, at 235 nm. Here, in (A) the dashed lines indicate the translational energy distributions for the fast and slow components for chlorine atom formation channel and the solid line shows the sum. The blue and red vertical arrows indicate the maximum available energy for the Cl ($^2P_{3/2}$) and Cl* ($^2P_{1/2}$) or Br ($^2P_{3/2}$) and Br* ($^2P_{1/2}$) elimination channels, respectively.
7.3.3 MULTIPHOTON IONIZATION OF HALOGENATED THIOPHENES

To understand the fragmentation pattern of the halogenated thiophenes to produce various mass ion peaks, mass spectrum in multiphoton ionization of halogenated thiophenes has been recorded at relatively high laser fluences. Apart from the REMPI lines of halogen atoms, many ion peaks, corresponding to the various fragments of halogenated thiophenes, have been observed in the multiphoton ionization process. In the case of 2-chlorothiophene, the mass spectrum shows various fragments in good agreement with the results by Xu et al.\textsuperscript{193}, in the positive and negative photoion spectroscopy studies using synchrotron vacuum ultraviolet radiation at 18 eV. In the multiphoton ionization/dissociation process at 235 nm, the parent ion and the various daughter ions are detected, as listed in Table 7.2. The natural isotope abundance ratio for $^{35}\text{Cl}/^{37}\text{Cl}$ is about 3:1, whereas $^{32}\text{S}:^{33}\text{S}:^{34}\text{S}:^{36}\text{S}$ is 95.02:0.75:4.21:0.02. Although we have observed all the isotopes for sulfur and chlorine atoms in the mass spectra, we have listed only the fragments with $^{35}\text{Cl}$ and $^{32}\text{S}$. Similarly, various ion fragments observed for 2-bromo-5-chlorothiophene have also been listed in Table 7.2.
**Table 7.2**: Various mass fragments observed in multiphotonic processes of 2-chlorothiophene and 2-bromo-5-chlorothiophene at 235 nm.

<table>
<thead>
<tr>
<th></th>
<th>2-Chlorothiophene</th>
<th>2-bromo-5-chlorothiophene</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>Fragment</td>
<td>m/z</td>
</tr>
<tr>
<td>32</td>
<td>S</td>
<td>32</td>
</tr>
<tr>
<td>39</td>
<td>C₃H₃</td>
<td>44</td>
</tr>
<tr>
<td>44</td>
<td>CS</td>
<td>56</td>
</tr>
<tr>
<td>45</td>
<td>CHS</td>
<td>57</td>
</tr>
<tr>
<td>57</td>
<td>C₂HS</td>
<td>68</td>
</tr>
<tr>
<td>58</td>
<td>C₂H₂S</td>
<td>69</td>
</tr>
<tr>
<td>69</td>
<td>C₃HS</td>
<td>73</td>
</tr>
<tr>
<td>73</td>
<td>C₃H₂Cl</td>
<td>79</td>
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<tr>
<td>79</td>
<td>CSCl</td>
<td>113</td>
</tr>
<tr>
<td>82</td>
<td>C₄H₂S</td>
<td>116</td>
</tr>
<tr>
<td>83</td>
<td>C₄H₃S</td>
<td></td>
</tr>
<tr>
<td>92</td>
<td>C₃HSCl</td>
<td></td>
</tr>
</tbody>
</table>
Molecular orbital (MO) calculations were carried out to generate the relative potential energy diagram for the dissociation channels of 2-chlorothiophene on its ground state. Calculations were done at G3B3 level of theory, using Gaussian suite of program. All the stationary points were calculated on the ground state, for various dissociation channels. Since G3B3 level of theory is not available for Br, the calculation was not done for 2-bromo-5-chlorothiophene, but we expect a similar type of mechanism for the brominated thiophene also. The G3B3 level of theory is very accurate, and is demonstrated by calculating the bond dissociation enthalpies of various heterocycles. In addition, it has the fewest convergence problems. In fact, the G3B3 level of theory calculates $\Delta H^{0}_{298}$, within an error of $\sim$1 kcal/mol, especially for halogenated heterocyles, such as halo thiophenes. We did not try to locate various transition states involved on the PES. Hence, we report here only the relative energy diagrams for various channels occurring on the ground PES of 2-chlorothiophene. The energy levels are schematically represented in FIG. 7.7, with the energy of each species marked in kcal/mol. The initial step is shown as either the cleavage of the C–Cl bond, forming thiophene radical and Cl atom, or that of the C–S bond. Since the two C–S bonds are not equivalent, their cleavage opens up the ring structure, forming two structures C–S1 and C–S2 (shown in FIG. 7.7). The C–S1 structure is more stable than the C–S2 by $\sim$ 1 kcal/mol, which indicates that it is harder to break the C–S bond, which involves the C atom attached to Cl atom. Similarly, for thiophene radical, it is harder to break the C–S bond that results in the formation of a radical having an odd electron located on carbon atom. This is reasonable, as the odd electron on the carbon atom overlaps with the lone electron pair of the sulfur atom, forming a stronger C–S.
to break. The thiophene radical formed, after the Cl atom elimination, can open up by the C–S bond cleavage, forming structures C–S3 and C–S4 (depicted in FIG. 7.7). These structures, C–S3 and C–S4, can also be formed from the primary structures, C–S1 and C–S2, by Cl atom elimination. However, these channels are well above the available photon energy of ~ 122 kcal/mol (FIG. 7.7). The structures C–S1 and C–S2 can also form various fragments, after a C–C bond cleavage. The C–S1 structure can produce acetylene and its co-fragments, whereas the C–S2 structure can form chloroacetylene and its various co-fragments, as shown in FIG. 7.7. However, no attempts were made to characterize the various transition states involved in the above reaction. From our calculations, it is clear that the formation of chloroacetylene seems to be more favorable than that of acetylene. Similarly, on the ground state of 2-chlorothiophene, the C–S bond cleavage is more favorable than the C–Cl bond cleavage. The C–Cl bond dissociation energy was estimated to be 98.8 kcal/mol in both the halogenated thiophenes. The C–Br bond dissociation energy in bromothiophene is estimated to be 91.2 kcal/mol, which is 7.6 kcal/mol lower than that of the C–Cl bond.199
FIG. 7.7: Relative energy diagram in kcal/mol, along with the structures, for various products in the photodissociation of 2-chlorothiophene at 235 nm in its ground state.
7.3.6 ESTIMATION OF $\Delta H_{298}^f$ VALUE FOR 2-CHLOROTHIOPHENE

The $\Delta H_{298}^f$ value for 2-chlorothiophene was estimated, using the following isodesmic processes.

$$\text{S} + \text{C}_4\text{Cl}_4 \rightarrow \text{S} \text{Cl} + \text{CHCl}_3 \quad (7.3)$$

$$\text{S} \text{Cl} + \text{CH}_4 \rightarrow \text{S} + \text{CH}_3\text{Cl} \quad (7.4)$$

The $\Delta H_{298}^0$ values for the above reactions were calculated at G3B3 level of theory, using Gaussian suite of program. Using the $\Delta H_{298}^f$ values for CCl$_4$, CH$_4$, CHCl$_3$, CH$_3$Cl and thiophene, the $\Delta H_{298}^f$ value of 2-chlorothiophene was estimated to be 24.1 and 23.0 kcal/mol, using reaction (7.3) and (7.4), respectively. Hence, the average $\Delta H_{298}^f$ value for 2-chlorothiophene can be given as 23.5 kcal/mol. The estimated $\Delta H_{298}^f$ value for 2-chlorothiophene is about 4.0 kcal/mol lower than that of thiophene. This trend is similar to that observed in benzene (19.8 kcal/mol) and chlorobenzene (13.0 kcal/mol), where the difference in $\Delta H_{298}^f$ values is about 6.8 kcal/mol. Considering the higher aromaticity of benzene ring than that of thiophene ring, the difference is reasonable and realistic. In addition, the inter-consistency in the calculation was verified by calculating the $\Delta H_{298}^0$ value for the following isodesmic reaction, involving the above species, and this calculated value matches very well with experimental data.

$$\text{CCl}_4 + \text{CH}_4 \rightarrow \text{CHCl}_3 + \text{CH}_3\text{Cl} \quad (7.5)$$

Hence, a $\Delta H_{298}^f$ value of 23.5 kcal/mole can be taken for 2-chlorothiophene, for further purposes.

7.4 DISCUSSION
7.4.1 NATURE OF EXCITATION AT 235 NM

The onset of optical absorption in thiophene is at about 5 eV (248 nm). Its gas phase UV absorption spectrum with $\lambda_{\text{max}} = 225$ nm (historically A band), has a long vibrational progression, with the band origin at 240 nm, for the lowest absorption. The nature of this band has been attributed to the vibrational origin of the $1^1A_1 \rightarrow 2^1A_1$ or the $\pi \rightarrow \pi^*$ transition. The gas phase UV absorption spectrum confirms the valence nature of this strong band at $\lambda_{\text{max}} = 225$ nm, extending up to 245 nm. On the other hand, UV-vis absorption of 2-chlorothiophene, with $\lambda_{\text{max}} \approx 235$ nm, extends up to 260 nm. However, it does not show any vibronic structure, like thiophene. Similarly, 2-bromo-5-chlorothiophene strongly absorbs at $\approx 245$ nm, and the absorption extends up to 270 nm. To understand the nature of the transitions involved in these halogenated thiophenes at 235 nm, ab initio molecular orbital (MO) calculations were performed, in detail, on these two compounds studied, along with thiophene. We optimized the ground state geometries of thiophene ($C_{2v}$), 2-chlorothiophene ($C_s$) and 2-bromo-5-chlorothiophene ($C_s$), employing density functional theory (DFT) calculation, using cc-pVDZ set of basis sets, maintaining their point group, as mentioned in the parenthesis. The augmented basis set, with diffuse and triple zeta functions, namely, aug-cc-pVTZ, was used for obtaining the vertical excitation energies for various transitions using time-dependent (TD) DFT. Although the calculated vertical transition energies slightly differ as compared to the experimental results, the nature of transitions and that of the orbitals involved are accurately predicted, using this method. The orbitals participating in the different electronic transitions were visualized, for better understanding of the process. The vertical excitation energies and the respective oscillator strengths of several low-lying singlet states of thiophene, 2-chlorothiophene and 2-bromo-5-chlorothiophene are shown in Table 7.3.
Table 7.3: Vertical excitation energies (eV) and oscillator strengths (given in parentheses) of low-lying singlet states of thiophene, 2-chlorothiophene and 2-bromo-5-chlorothiophene with respective designation. The $C_2v$, $C_s$ and $C_3$ symmetry designation of thiophenes, nature of transition and MO’s involved in the transitions are also indicated in the heading for thiophene, 2-chlorothiophene and 2-bromo-5-chlorothiophene.

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Thiope (C$_2$)</th>
<th>Vertical excitation energy (eV) and Oscillator strength (in parenthesis)</th>
<th>Excited State</th>
<th>2-Chlorothiophene (C$_s$)</th>
<th>Vertical excitation energy (eV) and Oscillator strength (in parenthesis)</th>
<th>Excited State</th>
<th>2-bromo-5-chlorothiophene (C$_3$)</th>
<th>Vertical excitation energy (eV) and Oscillator strength (in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>$1^1B_2$</td>
<td>$\pi \rightarrow \pi^*$ \hspace{1cm} 22 $\rightarrow$ 23 \hspace{1cm} 21 $\rightarrow$ 20 $\hspace{1cm}$ 5.73 (0.0796)</td>
<td>$S_1$</td>
<td>$2^1A'$</td>
<td>$\pi \rightarrow \pi^*$ \hspace{1cm} 30 $\rightarrow$ 31 $\hspace{1cm}$ 5.27 (0.1309)</td>
<td>$S_1$</td>
<td>$1^1A^*$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 47 $\rightarrow$ 49 $\hspace{1cm}$ 4.78 (0.0001)</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$2^1A_1$</td>
<td>$\pi \rightarrow \pi^*$ \hspace{1cm} 21 $\rightarrow$ 23 \hspace{1cm} 22 $\rightarrow$ 20 \hspace{1cm}$\lambda_{max} = 5.51$ eV \hspace{1cm} (Ref. 9)</td>
<td>$S_2$</td>
<td>$1^1A''$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 30 $\rightarrow$ 33 $\hspace{1cm}$ 5.55 (0.0005)</td>
<td>$S_2$</td>
<td>$2^1A'$</td>
<td>$\pi \rightarrow \pi^*$ \hspace{1cm} 47 $\rightarrow$ 48 $\hspace{1cm}$ 4.86 (0.2023)</td>
</tr>
<tr>
<td>$S_3$</td>
<td>$1^1A_2$</td>
<td>$\pi \rightarrow 3s$ \hspace{1cm} 22 $\rightarrow$ 24 $\hspace{1cm}$ 5.88 (0.0000)</td>
<td>$S_3$</td>
<td>$2^1A'$</td>
<td>$\pi \rightarrow 3s$ \hspace{1cm} 30 $\rightarrow$ 32 $\hspace{1cm}$ 5.63 (0.0016)</td>
<td>$S_3$</td>
<td>$2^1A'$</td>
<td>$\pi \rightarrow \sigma^*_c, 3s$ \hspace{1cm} 47 $\rightarrow$ 50, 51 $\hspace{1cm}$ 5.24 (0.0006)</td>
</tr>
<tr>
<td>$S_4$</td>
<td>$1^1B_1$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 22 $\rightarrow$ 25 $\hspace{1cm}$ 5.98 (0.0111)</td>
<td>$S_4$</td>
<td>$3^1A'$</td>
<td>$\pi \rightarrow \pi^*$ \hspace{1cm} 29 $\rightarrow$ 31 \hspace{1cm} 30 $\rightarrow$ 37 $\hspace{1cm}$ 5.76 (0.0677)</td>
<td>$S_4$</td>
<td>$3^1A'$</td>
<td>$\pi \rightarrow \pi^*$ \hspace{1cm} 46 $\rightarrow$ 48 \hspace{1cm} 47 $\rightarrow$ 54 $\hspace{1cm}$ 5.70 (0.0441)</td>
</tr>
<tr>
<td>$S_5$</td>
<td>$2^1A_2$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 21 $\rightarrow$ 25 $\hspace{1cm}$ 6.23 (0.0000)</td>
<td>$S_5$</td>
<td>$3^1A'$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 30 $\rightarrow$ 34 $\hspace{1cm}$ 5.89 (0.0043)</td>
<td>$S_5$</td>
<td>$3^1A'$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 47 $\rightarrow$ 50, 51 $\hspace{1cm}$ 5.72 (0.0007)</td>
</tr>
<tr>
<td>$S_6$</td>
<td>$2^1B_1$</td>
<td>$\pi \rightarrow 3s$ \hspace{1cm} 21 $\rightarrow$ 24 $\hspace{1cm}$ 6.27 (0.0005)</td>
<td>$S_6$</td>
<td>$4^1A'$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 29 $\rightarrow$ 33 $\hspace{1cm}$ 6.12 (0.0001)</td>
<td>$S_6$</td>
<td>$4^1A'$</td>
<td>$\pi \rightarrow \sigma^*_c$ \hspace{1cm} 46 $\rightarrow$ 49 $\hspace{1cm}$ 5.93 (0.0008)</td>
</tr>
</tbody>
</table>
The present computational results for thiophene are found to be in good agreement with the previous results\(^{183}\). So, we strongly believe that the present computational method can be well applied, to understand the excited states of 2-chlorothiophene and 2-bromo-5-chlorothiophene as well, and will provide very accurate data. Six excited states are considered, out of which, the four states are valence states and the remaining two are Rydberg states. For understanding the nature of initial excitation, only singlet states are considered because of their non-zero oscillator strengths. However, since the molecules contain heavy atoms like sulfur and bromine, the triplet states can also play a role in the photodissociation process because of efficient singlet-triplet cross-over. The various computed HOMO, LUMO and other MOs involved in the transition of all the above compounds are depicted in FIG. 7.8 and will be now discussed in brief. The valence states are primarily due to excitations from the \(\pi\) orbitals, mostly, HOMO and HOMO–1, to \(\pi^*\) orbitals, mostly, LUMO and LUMO+6, in all the cases. The other valence states are from the \(\pi\) orbitals to \(\sigma^*\) orbitals for thiophene, \(\sigma^*\) for 2-chlorothiophene and \(\sigma^*\) for 2-bromo-5-chlorothiophene. Besides these valence states, Rydberg states involving excitations to a diffuse 3s orbital are also included, for comparison. For 2-chlorothiophene, the \(S_1\) (\(2\,^1A'\)) state is still a \(\pi-\pi^*\) transition, with an oscillator strength of \(~0.13\) at 5.27 eV (235 nm). The second \(\pi-\pi^*\) transition is \(S_4\) (\(3\,^1A'\)), at 5.76 eV (215 nm), with an oscillator strength of \(~0.07\). The \(S_2\) (\(1\,^1A''\)) and \(S_3\) (\(2\,^1A''\)) are mainly \(\pi\rightarrow\sigma^*\) and \(\pi-3s\) transitions, respectively, with very low oscillator strengths \((~0.001)\), as compared to the \(\pi-\pi^*\) transition. Similarly, for 2-bromo-5-chlorothiophene, the \(S_1\) (\(1\,^1A''\)) state is a \(\pi\rightarrow\sigma^*\) transition at 4.78 eV (259 nm) with an oscillator strength value of \(~0.0001\). The \(S_2\) (\(2\,^1A'\)) and \(S_4\) (\(3\,^1A'\)) are \(\pi-\pi^*\) transitions at 4.86 eV (255 nm) and 5.70 eV (217 nm), respectively, with the
corresponding oscillator strengths of ~ 0.22 and ~ 0.046. The $S_3$ (2 $^1A''$), $S_5$ (3 $^1A''$) and $S_6$ (4 $^1A''$) are mainly $\pi$-$\sigma^*_{\text{C-S}, \text{C-Cl}}$, $\pi$-$\sigma^*_{\text{C-Br}}$, and $\pi$-$\sigma^*_{\text{C-S}}$ transitions, respectively, with an oscillator strength value of almost zero.

**FIG.7.8:** Computed HOMO, LUMO, along with other MOs involved in the transition of thiophene, 2-chlorothiophene, and 2-bromo-5-chlorothiophene at 235 nm.
Considering the corresponding wavelengths for vertical excitation energies and the respective oscillator strengths of the various transitions, it is evident that at 235 nm, all the three compounds have a $\pi$-$\pi^*$ transition. The excited state, with $\pi$-$\pi^*$ transition, adiabatically correlates only with highly excited photoproducts, and it is not feasible in a single-photon excitation in the present case. Therefore, it is assumed that, in the above two compounds, the initially prepared ($\pi\pi^*$) states cross over to the nearby states, mostly ($\pi\sigma^*$)$_{C_S, C_{Cl}, C_{Br}}$ state, from where the C–Cl/C–Br bond cleavages, forming Cl/Br atoms, and the ring opens by scission of the C–S bond. Also, the initially prepared ($\pi\pi^*$) or ($\pi\sigma^*$) state can undergo rapid internal conversion to the ground state, from where various other dissociation channels can occur, in addition to the above mentioned pathways from the excited state.

### 7.4.2 TRANSLATIONAL ENERGY RELEASE AND ANISOTROPY PARAMETER

In the photoexcitation of 2-chlorothiophene and 2-bromo-5-chlorothiophene at 235 nm, several processes have been proposed as primary dissociation pathways, and these are given as follows:

\emph{i) 2-chlorothiophene}

\[
\begin{align*}
\text{S-Cl} & \rightarrow \text{S}^* + \text{Cl} \quad \Delta H = 98.8 \text{ kcal/mol} \\
& \rightarrow \text{S--C(Cl)=CH--CH}=\text{CH} (C-S1) \quad \Delta H = 84.8 \text{ kcal/mol} \\
& \rightarrow \text{S--CH=CH--CH=C--Cl} (C-S2) \quad \Delta H = 85.5 \text{ kcal/mol}
\end{align*}
\]  

As discussed earlier, $\Delta H$ values are calculated at G3B3 level of theory. The reaction (7.6) involves the cleavage of the C–Cl bond, while reactions (7.7) and (7.8) involve ring opening of thiophene structure, by C–S bond cleavage, forming two different
types of biradicals, namely, \( C-S1 \) and \( C-S2 \), as discussed earlier. The Cl atom can be produced directly as a primary product, as in reaction (7.6), and also from the subsequent dissociation of the biradicals, \( C-S1 \) and \( C-S2 \), as shown below.

\[
S-\text{C(Cl)}=\text{CH}-\text{CH}=\text{CH} \quad (C-S1) \rightarrow S=\text{C}=\text{CH}-\text{CH}=\text{CH} \quad + \quad \text{Cl} \quad \Delta H = 45.0 \text{ kcal/mol} \quad \text{(7.9)}
\]

\[
S-\text{CH}=\text{CH}-\text{CH}=\text{C}=\text{Cl} \quad (C-S2) \rightarrow S-\text{CH}=\text{CH}-\text{CH}=\text{C} \quad + \quad \text{Cl} \quad \Delta H = 69.2 \text{ kcal/mol} \quad \text{(7.10)}
\]

The subsequent formation of Cl atom, after the initial C–S bond cleavage, is ruled out in present experimental condition due to its high endothermicity. Hence, the formation of Cl atom is possible only from the cleavage of the C–Cl bond in the parent molecule itself, as depicted in reaction (7.6). In following paragraphs, the initial C–X bond rupture process on the ground or from an excited potential energy surface is discussed, depending on the dynamics of the processes.

The two types of \( P(v) \) or \( P(E_T) \) were observed for Cl\((^3P_{3/2})\), in the C–Cl bond fission, one producing fragments with relatively higher recoil energies and the other producing fragments with lower recoil energies. The \( P(E_T) \) for the high-translational energy component peaks near 3 kcal/mol, and extends up to ~17 kcal/mol (FIG. 7.6[A]). Similarly, the low translational energy component peaks near 1 kcal/mol, and extends up to ~3 kcal/mol. The presence of two types of \( P(E_T) \) in the C–Cl bond fission is analogous to other systems involving a \( \pi-\pi^* \) transition. On the contrary, only one type of \( P(v) \) or \( P(E_T) \) was observed for Cl\(^*\)(\( ^2P_{1/2} \)) formation channel, which peaks near 4 kcal/mol, and extends up to ~18 kcal/mol (FIG. 7.5[B]). Although in the case of substituted halo thiophenes, the transitions at 235 nm are purely \( \pi-\pi^* \) in nature, the molecule can predissociate after crossover to the nearby C–Cl repulsive state. It is
also possible that the other translational energy channel having lesser $E_T$, results from the C–Cl fission, following internal conversion to the ground electronic state.

The partitioning of the available energy into various degrees of freedom of the fragments is mainly governed by the nature of the dissociative potential energy surface, and can be predicted, using simple models, such as impulsive and statistical. It is well known that the energy partitioning in a dissociative event on a repulsive surface is well described by an impulsive model\(^{121}\). In this model, the distribution of energy among the product states is governed by the dissociative event, i.e., by the repulsive force acting during the breaking of the parent molecule into the fragments. For example, in the present case, by using only conservation of momentum and energy, and the impulse assumption, one finds that the fraction of the available energy ($E_{avl}$) released as translational energy is given by

$$E_T = \left( \frac{\mu_{C,Cl}}{\mu_{C-(C_4H_3S),Cl}} \right) E_{avl}, \quad \text{and} \quad f_T = \frac{E_T}{E_{avl}}$$

(7.15)

where $\mu_{C,Cl}$ is the reduced mass of the C and Cl atoms, $\mu_{C-(C_4H_3S),Cl}$ is the reduced mass of the thiophene radical, $c-(C_4H_3S)$ and Cl, $E_{avl}$ is the available energy and $f_T$ is the fraction of the available energy going into the translational modes of the fragments. For 2-chlorothiophene, the ratio of the reduced masses is 0.36. The available energy is given by,

$$E_{avl} = E_{hv} - D_0^0(c - C_4H_3S - Cl) - E_{SO}$$

(7.16)

where $E_{hv}$ is the photon energy (122.0 kcal/mol), $D_0^0(c - C_4H_3S - Cl)$ is the C–Cl bond dissociation energy, and $E_{SO}$ is the spin-orbit energy of chlorine (2.4 kcal/mol). The bond dissociation energy is taken as 99.0 kcal/mol. Thus, $E_{avl}$ value for the Cl and Cl* channels are 23.0 and 20.6 kcal/mol, respectively. The experimental average translational energies ($E_T$) for the fast and slow components are found to be 3.0±1.0
and 1.0±0.5 kcal/mol, respectively, for Cl channels, giving the $f_T$ values of 0.13 and 0.04. Thus, the experimentally determined $f_T$ value is considerably lower than the predicted value of 0.36, using the impulsive model. Similarly, a $f_T$ value of 0.17 is determined for Cl* channel. The much lower experimental $f_T$ value obtained in the dissociation of 2-chlorothiophene, as compared to the predicted value using impulsive model, prompted us to apply the statistical model also, as discussed in following paragraph.

A statistical dissociation process occurs predominantly, if the photo-excited parent molecule is so long-lived that the excess energy is partitioned statistically amongst the available degrees of freedom of the products. This may be applicable in a process wherein a rapid internal conversion to the ground electronic state takes place, followed by the subsequent slow dissociation. Under these circumstances, in a large molecule, with many low frequency modes, a relatively small amount of the excess energy is partitioned into translational motion of the products. For this kind of dissociation process, *a priori* calculations\textsuperscript{118,200} were adopted, along with a simple analytical expression established by Klots\textsuperscript{120}, relating the mean translational energy release, $E_T$, and the $E_{avl}$, for a statistical barrier-less dissociation process. These statistical methods predict a $f_T$ value of ~0.06, which matches well with the experimental value of 0.04, for the slow component. This implies that the slow component of Cl is mainly due to the dissociation process, taking place on the ground state potential energy surface, after internal conversion via some curve crossing mechanism. The measured $f_T$ value of 0.13, for the faster component of the Cl atom channel, is higher than the predicted statistical. Similarly, the measured $f_T$ value (0.17) for the Cl* channel, lies in between the values predicted by the impulsive and
statistical models. Thus, the fast component of Cl and Cl* formation channel does not occur on the ground state potential energy surface.

In the present case, the impulsive model does not predict well the experimental results. One of the reasons for such a failure of the impulsive model may be assigned to the scenario, similar to that in CCl$_4$. In CCl$_4$, it is proposed that an extensive internal vibrational redistribution takes place, before enough energy is localized in one bond. Consequently, in photodissociation of CCl$_4$ at 234 nm, the $f_T$ values predicted, using impulsive and statistical models, are 0.33 and 0.13, respectively, whereas the experimental $f_T$ value is 0.10, for both Cl and Cl*. However, a small contribution from the high energy $E_T$ component was observed in the Cl* channel. In halogenated thiophenes, as discussed earlier, the initial excitation is pure $\pi-\pi^*$ in nature. Hence, to dissociate a C–X bond, an extensive internal vibrational redistribution must take place to localize enough energy in the C–X bond in the crossover process from the ($\pi\pi^*$) state to the nearby ($\pi\sigma^*$) state. This process is in complete contrast to the impulsive model assumption.

Another possible reason for deviation of the measured $f_T$ value from the impulsive value can be the error involved in the experimental determination of translational energy. Since the $E_{av}$ is much lower in all the cases, due to high $D_0^*$ for the various channels, the width of TOF profile is comparable with the instrumental function width. Due to this reason, the error involved in the determination of $E_T$ is slightly higher, and may change the $f_T$ values considerably. However, the $f_T$ values for Cl* and the fast component of Cl are much higher than the values predicted using statistical model. Therefore, we strongly believe that the dynamics of the fast Cl and Cl* formation takes place on the higher excited states, and not on the ground state. Another valid and strong reason to believe the excited state dissociation dynamics for
the fast Cl and Cl\(^*\) formation lies in the \(f_T\) values for Cl\(^*\). A careful examination reveals that the \(f_T\) value for Cl\(^*\) (0.17) is higher than that for the Cl fast channel (0.13), despite its low \(E_{\text{av}}\). If the dissociation occurs on the ground state potential energy surface, then the \(f_T\) value is expected to be the same for both Cl and Cl\(^*\). Also, the relative quantum yield, \(\Phi(\text{Cl}^*)\), which is 0.19 for 2-chlorothiophene, deviates significantly from its statistical limit (0.33). Finally, the above discussion concludes that the initially prepared 2-chlorothiophene in the (\(\pi\pi^*\)) state crosses over to the nearby (\(\pi\sigma^*\))\(_C^{}\text{Cl}\) state, and subsequently the C–Cl bond cleavage occurs, resulting in the formation of the fast Cl atom.

\textit{ii) 2-bromo-5-chlorothiophene}

\[
\begin{align*}
\text{Br} & \text{S} \text{Cl} \rightarrow \text{Br} & \text{S} & \text{Cl}^* & + & \text{Cl} \quad \Delta H = 98.8 \text{ kcal/mol} \\
(7.11) \\
\rightarrow & \text{S} & \text{Cl} & \text{Br} & + & \text{Br} \quad \Delta H = 91.2 \text{ kcal/mol} \\
(7.12) \\
\rightarrow & \text{S} – \text{C(Br)} = \text{CH} – \text{CH} = \text{C} – \text{Cl} \quad \Delta H = \sim 86.0 \text{ kcal/mol} \\
(7.13) \\
\rightarrow & \text{S} – \text{C(Cl)} = \text{CH} – \text{CH} = \text{C} – \text{Br} \quad \Delta H = \sim 86.0 \text{ kcal/mol} \\
(7.14)
\end{align*}
\]

In the case of 2-bromo-5-chlorothiophene, the reaction (7.11) involves cleavage of C–Cl bond, while the reaction (7.12) involves cleavage of the C–Br bond, forming Cl and Br atoms, respectively. The reactions (7.13) and (7.14) are involved in the ring opening of thiophene structure, with the cleavage of the C–S bond, forming two
different types of biradicals. The subsequent formation of Cl/Br atoms from these biradicals is ruled out energetically. Hence, the formation of halogen atom is attributed to the initial cleavage of the C-X bond directly from the parent molecule, similar to that in 2-chlorothiophene.

For 2-bromo-5-chlorothiophene, only one type of $P(v)$ or $[P(E_T)]$ was observed for all the halogen atom fragments detected. The $P(E_T)$ for Cl ($^2P_{3/2}$) derived from the forward convolution fit peaks near 3.5 kcal/mol, and extends up to ~17 kcal/mol. The $P(E_T)$ for Cl* ($^2P_{1/2}$) channel peaks near 5 kcal/mol, and extends up to ~18 kcal/mol. Similarly, for Br atom elimination channel, the $P(E_T)$ peaks near 2 kcal/mol, and extends up to ~14 kcal/mol. For Br* channel, it peaks near 3.6 kcal/mol, and extends up to ~15 kcal/mol. For this halogenated thiophene as well, the $f_T$ values for Cl (0.15) and Cl* (0.24) elimination channel, are much higher than the values predicted using statistical model (0.06), and lower than that predicted, using impulsive model (0.31). In the present case, the measured $f_T$ value (0.24) for Cl* is closer to the value predicted, using the impulsive value (0.31). A similar trend is also observed in the case of Br atom elimination channel. The $f_T$ value (0.17) for Br* matches very well with the value predicted, using impulsive model (0.22), within experimental uncertainties. Although, for Br atom, the $f_T$ value matches very well with the statistical value, the formation of Br atom is believed to be from the excited state only, as discussed earlier for slow component of Cl of 2-chlorothiophene. Also, the $P(E_T)$ for Cl(Cl*) and Br(Br*) extend up to the total available energy, with non-Maxwell-Boltzmann type of distribution having a large width. Here also, if the molecule relaxes to the ground state, the most favorable process would be the C–S bond cleavage, which opens up the ring structure. However, the formation of Br on ground state potential energy surface is not totally ruled out. The details of the $E_T$ and
For all the channels of 2-bromo-5-chlorothiophene, along with that of 2-chlorothiophene, are given in Table 7.4.

**Table 7.4:** The average translational energy, $\langle E_T \rangle$, available energy ($E_{avl}$), $f_T$ value, and the relative quantum yield of spin-orbit states ($\Phi$) for photodissociation of 2-chlorothiophene and 2-bromo-5-chlorothiophene at $h\nu=235$ nm. The excitation energy is 122 kcal/mol. The $D_0^0$(C–X) for Cl and Br elimination channel is taken as 99.0 and 91.0 kcal/mol, respectively. All energies are in kcal/mol.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Channel</th>
<th>$\langle E_T \rangle$</th>
<th>$E_{avl}$</th>
<th>$f_T=\langle E_T \rangle/E_{avl}$</th>
<th>Relative quantum yield ($\Phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
<td>Impulsive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-chlorothiophene</td>
<td>Cl</td>
<td>3.0±1.0</td>
<td>23.0</td>
<td>0.13</td>
<td>0.36(0.06)</td>
</tr>
<tr>
<td></td>
<td>Slow</td>
<td>1.0±0.5</td>
<td></td>
<td>0.04</td>
<td>0.36(0.06)</td>
</tr>
<tr>
<td></td>
<td>Cl*</td>
<td>3.5±1.0</td>
<td>20.6</td>
<td>0.17</td>
<td>0.36(0.06)</td>
</tr>
<tr>
<td>2-bromo-5-chlorothiophene</td>
<td>Cl</td>
<td>3.5±1.0</td>
<td>23.0</td>
<td>0.15</td>
<td>0.31(0.06)</td>
</tr>
<tr>
<td></td>
<td>Cl*</td>
<td>5.0±1.5</td>
<td>20.6</td>
<td>0.24</td>
<td>0.31(0.06)</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>2.0±1.0</td>
<td>31.0</td>
<td>0.06</td>
<td>0.22(0.06)</td>
</tr>
<tr>
<td></td>
<td>Br*</td>
<td>3.6±1.0</td>
<td>20.5</td>
<td>0.17</td>
<td>0.22(0.06)</td>
</tr>
</tbody>
</table>

Very recently, Wang and co-workers \(^{194}\) studied the dynamics of Br atom formation in the photodissociation of bromothiophenes, namely, 2-bromothiophene and 3-bromothiophene, at 267 nm, using ion velocity imaging technique. The Br/Br* channel in these studies showed multiple components in the translational energy distribution, P($E_T$). The $f_T$ values were estimated as large as 0.96. In addition, they have shown anisotropy in the products. All these results completely contradict our
findings in photodissociation of 2-bromo-5-chlorothiophene for Br/Br* elimination channel at 235 nm. In their results, the P(E_T) overshoots the available energy, for some of the components, despite a lower value of ~73 kcal/mol was used for the $D_0^0(c - C_4H_3S - Br)$ bond dissociation energy, which is almost 18 kcal/mol less than the value recommended recently, and also used by us\textsuperscript{199}. This discrepancy may be due to some contribution from the multiphotonic processes in their studies.

In the limit of an instantaneous dissociation process, the parameter $\beta$ is given by $\beta = 2\langle P_2(\cos \theta_m) \rangle$, where $\theta_m$ is the molecular frame angle between the molecular transition dipole moment and the photofragment recoil direction, and $P_2(\cos \theta_m)$ is the second order Legendre polynomial. Hence, for a parallel or a perpendicular transition, one would expect anisotropy of +2 or -1, respectively. The recoil anisotropy, $\beta$, for the all the halogen atom fragments, measured in the present work is ~0.0, which indicates an isotropic dissociation process. This value of $\beta$ does not give any indication of the nature of the transition dipole moment in dissociation of halogenated thiophenes. As discussed in our previous work\textsuperscript{202}, the anisotropy in an impulsive dissociation can be reduced, or wiped out, due to several factors, such as mixed initial excitation with both parallel and perpendicular components, longer dissociation lifetime, dissociation not occurring from a single geometry rather from a range of geometries, etc. In halogenated thiophenes, with C\textsubscript{s} geometry, for the $\pi-\pi^*$ transition, with $^1A'$ symmetry, the transition dipole moment is mainly along x- and y- direction. However, for the ($\pi\sigma^*$) state, with $^1A''$ symmetry, the transition dipole moment is mainly along z-direction. Therefore, in the present case, for the formation of Cl and Br atoms, the molecule has to cross over from the initially prepared ($\pi\pi^*$) state to the ($\pi\sigma^*$) state. During this crossover period, the molecule may rotate. The absence of recoil anisotropy in the present studies is expected mainly due to the relatively longer
dissociation lifetime, since the dissociation is not from the initially prepared state, rather from the crossover state.

7.5 CONCLUSION

The photodissociation of two halogenated thiophenes, namely, 2-chlorothiophene and 2-bromo-5-chlorothiophene, has been carried out at around 235 nm, and the dynamics of C–X (X=Cl, Br) bond dissociation is investigated, using resonance-enhanced multiphoton ionization, coupled with a time-of-flight mass spectrometer. The excitation at 235 nm prepares the molecules in the (ππ*) state. We have determined the photofragment speed distribution, the anisotropy parameter β and the spin-orbit branching ratio, for chlorine and bromine atom elimination channels, to gain insights into the dynamics of halogen atom formation. Polarization-dependent and state-specific TOF profiles are utilized, to get translational energy distributions, using a forward convolution method and taking into account the fragment anisotropies. The anisotropy parameters for both Cl(Cl*) and Br(Br*) are the same, and characterized by values of 0.0±0.05. In the translational energy distribution for the chlorine atom elimination channel in the case of 2-chlorothiophene, we have observed two components for Cl, but only one component for the Cl*. The average translational energies for the fast and the slow components of the Cl channel are 3.0±1.0 and 1.0±0.5 kcal/mol, respectively. For Cl*, the average translational energy is 3.5±1.0 kcal/mol. However, for 2-bromo-5-chlorothiophene, we have observed only one component for all the halogen atom channels in translational energy distribution. The average translational energies for the Cl and Cl* channels are 3.5±1.0 and 5.0±1.0 kcal/mol, respectively. Similarly, the average translational energies for the Br and Br* channels are 2.0±1.0 and 3.5±1.0 kcal/mol, respectively. The partitioning of energy into the translational modes is interpreted with the help of various models,
such as impulsive and statistical models. The $\Delta H^\circ_{f}$ value for 2-chlorothiophene is estimated theoretically to be 23.5 kcal/mol.