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INTRODUCTION:

Photodissociation, often termed as second half of a full collision, is the formation of two (or more) fragments following absorption of light by a molecule. Upon photoexcitation, a molecule can undergo several photophysical and photochemical processes. Among them, in gas phase, perhaps the most investigated process is the unimolecular photodissociation of polyatomic molecules [1], as this is the initiation of many chemical reactions in the atmosphere. In recent times the gas phase photodissociation of halogenated polyatomic molecules has attracted immense interest mainly due to their active role in stratospheric ozone depletion. Several experimental and theoretical studies have been devoted to understand these molecular dissociation processes. Measurement of different microscopic details, like partitioning of the available energy among different states of a photofragment often point to the mechanism of the reaction. Combining the experimentally obtained information with the results of theoretical calculations can help in fundamental level understanding of a photodissociation process.

The nature of chromophore present and the initially prepared excited state often dictate the fate of the photodissociation dynamics and product state distribution. For example, the UV excitation of the $\sigma^*(C-X)\rightarrow n(X)$ transition of monohalogenated alkanes generally leads to impulsive C-X bond cleavage, producing the halogen radical in both its ground state $X(^3P_{3/2})$ and spin orbit excited state $X^*(^3P_{1/2})$ with different branching ratios and recoil anisotropy. However for alkyl halides with multichromophores, various additional dissociation channels can operate with
different branching ratios, depending on the nature of excitation and the presence of a functional group. Therefore, the studies on photodissociation dynamics of alkyl halides with multihalogen atoms and other functional groups are being pursued actively [2]. In this thesis we have investigated the UV-photodissociation of halogenated compounds with various functional groups to understand the role of chemical environment and nature of the initial excited state, on the C-X and N-OH bond dissociation dynamics. The thesis consists of seven chapters for a clear presentation of the work and explained briefly in the following paragraphs.

CHAPTER 1

This is an introductory chapter giving a general overview of photodissociation dynamics and its importance. The methods of photoexcitation, followed by the fate of the excited molecule, are discussed with a focus on photodissociation processes. A brief discussion on the essence of photodissociation dynamics study and its development is also highlighted. Various aspects of a photodissociation process, like potential energy surfaces of reactants and products, partitioning of the available energy into internal states of the nascent products, and the models available for explaining this distribution, are discussed. Since, theoretical calculation is employed to aid interpretation of the experimental results, a brief on the computational chemistry, \textit{ab initio} molecular orbital calculations and semi-empirical calculations employing Gaussian 03 programme [3], is also discussed.

CHAPTER 2

This chapter gives a brief account of the experimental techniques and instrumentation employed to execute the work. Two very sensitive and selective, Molecular Beam-Resonance Enhanced Multiphoton Ionisation-Time of Flight Mass
Spectrometry (MB-REMPI-TOFMS) and Laser Photolysis-Laser Induced Fluorescence (LP-LIF) techniques have been used to detect transient species and to obtain the dynamical information. The LP-LIF experiments were carried out in a flow system, and REMPI experiments in a molecular beam environment.

REMPI was used to detect the halogen atoms, Cl/Br ($^2P_{3/2}$) and Cl*/Br* ($^2P_{1/2}$), and HCl in their nascent states. A single laser beam near 235 nm was employed for photodissociation of parent molecules as well as ionization of the photoproducts. The OH fragment was probed by exciting its $A^2\Sigma^+ \rightarrow X^2\Pi$ system (306-309 nm), using a tunable dye laser and monitoring the subsequent A→X fluorescence.

CHAPTER 3

In this chapter the photodissociation dynamics of 2-bromo-2-chloro-1,1,1-trifluoroethane (halothane) on excitation of the $\sigma^*(C-Br) \leftrightarrow n(Br)$ transition near 234 nm is reported [4]. These studies are aimed at investigating the effect of the Cl atom on the dynamics of the expected C-Br bond scission in halothane. In addition, we were interested in exploring the possibility of the stronger C-Cl bond cleavage. The experiment was carried out in a molecular beam environment, employing REMPI-TOF-MS setup. Analogous to saturated alkyl halide dissociation, the C-Br bond scission is observed predominantly due to direct $\sigma^*(C-Br) \leftrightarrow n(Br)$ transition. However, the formation of chlorine atom with a considerable value of recoil anisotropy parameter $\beta$ is interesting, since it signifies intramolecular energy transfer from one repulsive state [$n,\sigma^*(C-Br)$] to another [$n,\sigma^*(C-Cl)$]. The details of the chlorine (bromine) atom formation channel and the effect of bromine (chlorine) atom on the overall dynamics of halothane dissociation are discussed in this chapter. The velocity distribution of bromine atom has one component, however, that of chlorine
atom is bimodal. Both fast and slow chlorine atom channels, with the $\beta$ value of $0.3\pm0.1$, are produced impulsively from the $[n,\sigma^*(C-\text{Cl})]$ repulsive surface, indicating a fast energy transfer to the C-Cl channel from the initial excited state.

**CHAPTER 4**

This chapter deals with the details of the UV-photodissociation of tetrachloroethylene in a supersonic molecular beam at ~235 nm [5]. The principal objective of the work was to understand the dynamics of the C-X bond scission in an unsaturated alkyl halide, which has many low energy excited states. Tetrachloroethylene was selected as a representative molecule to investigate the C-Cl bond dissociation.

UV excitation of saturated alkyl halides, e.g. halothane discussed in chapter 3, generally leads to the C-X (X=Cl / Br) bond fission from a repulsive state $[n,\sigma^*(C-X)]$ with an impulsive mechanism, producing X and X* with an anisotropic angular distribution. However, the dynamics of the C-X bond fission in unsaturated alkyl halides is totally different, and depends upon the nature of the excited state. In this regard dissociation dynamics of chloroethylenes are interesting due to the presence of multiple pathways, which can get altered depending on the excitation wavelength, including simple bond cleavage, molecular eliminations and three body dissociation processes. In this work we have determined the center-of-mass photofragment speed distribution, recoil anisotropy parameter ($\beta$), and the spin-orbit branching ratio for chlorine atom elimination channels. Two components, namely, the fast and the slow, are observed in the translational energy distributions of Cl and Cl*. The average translational energies for the Cl and Cl* channels for the fast components are $17.6\pm1.9$ and $14.0\pm1.7$ kcal/mol, while that for the slow components are $2.2\pm1.0$ and $3.2\pm1.0$
kcal/mol, respectively. Detailed theoretical calculations are performed using Time-dependent Density Functional Theory (TD-DFT) method to understand the nature of the dissociative potential energy surface involved in the chlorine atom formation channel. Here, the bound nature of the $\pi\sigma^*(C-Cl)$ state in chloroethylenes is reported. Finally, it is concluded that the high translational energy component of the chlorine atom channel is coming from the $[\pi,\sigma^*(C-Cl)]$ surface. Whereas, the lower energy component is mainly due to internal conversion from the $[\pi,\sigma^*(C-Cl)]$ state to the ground state, that dissociates statistically.

**CHAPTER 5**

This chapter provides the details on photodissociation dynamics of 2-furoyl chloride [6] and benzoyl chloride [7] in a supersonic molecular beam at around 235 nm. These two molecules are selected as representative aromatic acyl halides, which have COCl moiety in their side chain, to investigate the dynamics of the C(O)-Cl bond dissociation. In general the gas-phase dissociation of acyl halides in the UV region is dominated by the C-Cl bond cleavage through the diabatic interactions between the initially excited $[n,\pi^*(CO)]$ or $[\pi,\pi^*(CO)]$ state and $[n,\sigma^*(C-Cl)]$ repulsive state. Fast diabatic interactions between $[n,\pi^*(CO)]$ and $[n,\sigma^*(C-Cl)]$ have been reported, which lead to chlorine atom generations with high kinetic energy and non-zero value of recoil anisotropy parameter, $\beta$. However, in the present work on 2-furoyl chloride and benzoyl chloride, chlorine atoms were formed isotropically ($\beta=0$) in both their ground and the spin orbit excited states with bimodal translational energy distributions. The observed branching ratio of the high to low energy chlorine component in benzoyl chloride (0.72/0.28) is slightly different from that in 2-furoyl chloride (0.78/0.22). The results suggest that the electronic relaxation to the vibrationally excited ground state in
benzoyl chloride is more efficient than that in 2-furoyl chloride. One major difference in the dissociation dynamics of these two compounds is the presence of the molecular HCl elimination channel in benzoyl chloride. Apart from the HCl channel, the overall dynamics of dissociation of benzoyl chloride and 2-furoyl chloride are similar, and the dissociation takes place only in the side chain. On excitation at 235 nm benzoyl chloride and 2-furoyl chloride are initially excited to the \( S_3 \left( ^1\pi,\pi^* \right) \) and \( S_2 \left( ^1\pi,\pi^* \right) \) states, respectively, from where a major fraction relaxes to the \( S_1 \left( ^1\pi,\pi^* \right) \) state to produce the high kinetic energy chlorine atom channel, and a minor fraction relaxes to the ground (\( S_0 \)) state to produce the slow chlorine channel.

**CHAPTER 6**

In this chapter the details of UV-photodissociation of 2-bromo-2-nitropropane (BNP) is discussed [8]. The previous chapters in this thesis were focused on the dynamics of halogen atom formation on UV excitation of different halogenated molecules, and the role played by the nature of initial excited states in controlling the overall dynamics of the C-X bond dissociation. However, the presence of a halogen atom itself can significantly alter the dynamics of dissociation of a polyatomic organic molecule by changing the nature of excitation of the molecule, and providing various low energy dissociation pathways. Our interest was to investigate the effect of a halogen substituent on the dissociation dynamics of a nitrocompound, for which BNP is selected.

Photoexcitation of BNP at 248 and 193 nm generates OH, Br and NO\(_2\) among other products. The OH fragment is detected by laser-induced fluorescence spectroscopy, and its translational and internal state distributions are probed. At both 248 and 193 nm, the OH fragment is produced translationally hot with the energy of
10.8 and 17.2 kcal/mol, respectively. However, it is produced vibrationally cold ($v''=0$) at 248 nm, and excited ($v''=1$) at 193 nm with a vibrational temperature of 1870±150 K. It is also generated with rotational excitation, rotational populations of OH($v''=0$) being characterized by a temperature of 550±50 and 925±100 K at 248 and 193 nm excitation of BNP, respectively. The NO$_2$ product is produced electronically excited at 193 nm, as detected by measuring UV-visible fluorescence, and mostly in the ground electronic state at 248 nm. The Br product is detected employing resonance-enhanced multiphoton ionization with time-of-flight mass spectrometer. The average translational energies for the Br and Br* channels are 5.0±1.0 and 6.0±1.5 kcal/mol. No recoil anisotropies were observed for these products. Most plausible mechanisms of OH and Br formation are discussed based on both the experimental and the theoretical results. The electronically excited BNP molecules at 248 and 234 nm relax to the ground state, and subsequently dissociate to produce OH and Br through different channels. The mechanism of OH formation from BNP on excitation at 193 nm is also discussed.

CHAPTER 7

This chapter provides a summary to the work carried out in this thesis, and a future direction to this work to acquire assistive knowledge. The thesis presents details on dynamics of UV dissociation of several halogenated molecules with atmospheric relevance. The effect of various substituents on photodissociation has been investigated by probing the nascent photoproducts (mostly halogen atom and OH), employing LIF and REMPI techniques in a collision-free condition. Various scalar and vector quantities of dissociation have been measured, and corroborated by theoretical modelling and molecular orbital calculations.
Halothane, a saturated alkyl halide, undergoes the impulsive C-Br bond cleavage, as expected, on excitation of the $\sigma^*(C-Br) \leftrightarrow \pi(Br)$ transition at 235 nm. However, unexpectedly the stronger C-Cl bond also cleaves due to the energy transfer from the $[\pi, \sigma^*(C-Br)]$ state to the $[\pi, \sigma^*(C-Cl)]$ state. The presence of the bromine atom has a pronounced effect on the C-Cl bond dissociation dynamics. The energy transfer between these two modes is fast enough to produce anisotropic distribution of the chlorine atoms. In case of tetrachloroethylene, however, presence of unsaturation modifies the initial transition at 235 nm to the $[\pi, \sigma^*(C-Cl)]$ state, from where fast chlorine is produced. In addition, a slow chlorine atom channel is observed from the ground state of tetrachloroethylene, formed after fast internal conversion. Both chlorine atom channels are associated with a slow dissociation. In halogenated molecules of benzoyl and 2-furoyl chlorides, with carbonyl group and extended conjugation, the initial excitation at $\sim$235 nm leads to the $|1\pi, \pi^*\rangle$ state with the initial excitation localized in the carbonyl group. The initially excited state produces mainly the high kinetic energy chlorine atom channel, and a minor fraction relaxes to the ground state ($S_0$) to produce the slow chlorine atom channel. The overall C-Cl bond dissociation dynamics is similar in both the molecules. However, in benzoyl chloride a molecular HCl elimination channel was observed, which is not feasible energetically in 2-furoyl chloride. For a halogenated molecule with a nitro group, such as 2-bromo-2-nitropropane (BNP), the dynamics of dissociation is very much different. At 248 nm the BNP molecule is excited to the $(n, \pi^*)$ state from where it relaxes to the ground state, and subsequently dissociates to produce OH and Br through different channels. At 193 nm the initial excitation is located at C-Br bond $(n, \sigma^* \text{state})$, from where BNP molecules can undergo repulsive C-Br bond scission, and subsequently the co-
fragment of Br can dissociate producing OH after intramolecular re-arrangement. Alternatively, the mechanism of OH formation can remain similar as that proposed for the dissociation of BNP at 248 nm excitation.

**FUTURE DIRECTIONS**

The work reported in the thesis employing REMPI technique has been carried out by single laser beam. Better information about the excited PESs, and their interaction can be deduced by performing experiments at different frequencies of the pump laser, and using velocity map imaging. Our main objective was to measure the scalar dynamical quantities like, internal energy distribution, spin-orbit ratio, doublet ratio, etc. associated with OH formation for understanding OH formation dynamics in photodissociation of polyatomic molecules. One may obtain additional information on the dynamics by performing polarization experiments and detecting the vector quantities, like angular distribution of the OH photofragment etc.

We have explained our experimental results satisfactorily with theoretical calculations at relatively lower level, because of computation resource constraints. The associated error level in energy calculations can be further reduced by performing calculations at higher level with larger basis sets.
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**FIG. 1.1:** Photophysical processes of an excited polyatomic molecule in gas phase. Vertical straight lines represent radiative transitions, wavy lines represent non-radiative transitions.

**FIG. 1.2:** Direct and indirect photodissociation processes of diatomic molecules.

**FIG. 1.3:** Two additional types of photodissociation processes of diatomic molecules.

**FIG. 1.4:** Schematic of laser photolysis-laser induced fluorescence technique.

**FIG. 1.5:** Schematic of REMPI schemes: a) One color (1+1) REMPI; b) One color (2+1) REMPI; and c) Two color (3+1) REMPI. $S_i$, $S_f$, and IC denote the initial ground state, resonant excited state and the ionization continuum, respectively.

**FIG. 1.6:** Energy partitioning, using hybrid model, for the dissociation process $^{\text{hv}} \text{A—BC} \rightarrow \text{A + BC}$.

**FIG. 1.7:** Different vector correlations in photodissociation dynamics. The transition dipole vector, $\mu$, is correlated both with $v$ and with $J$. Consequently, $v$ and $J$ are correlated even there is no $E$-$v$ or $E$-$J$ correlation.

**FIG. 2.1:** Experimental setup of Laser photolysis laser induced fluorescence technique.

**FIG. 2.2:** Flow chart of obtaining the dynamics of photodissociation process from LIF data.
FIG. 2.3: Schematic of molecular beam-resonance enhanced multiphoton ionization-time of flight mass spectrometry (MB-REMPI-TOF-MS) setup.

FIG. 2.4: Dependence of the REMPI signal of HCl, formed during photolysis of benzoyl chloride, on the laser intensity.

FIG. 2.5: (2+1) REMPI scheme for Cl and Cl* detection.

FIG. 2.6: (2+1) REMPI scheme for Br and Br* detection.

FIG. 2.7: Schematic of the ion source. Plate f_1, f_2 and f_3 stands for the repeller plate, extraction and acceleration grid, respectively.

FIG. 2.8: Plot of arrival time (μs) for various fragments (m/z) for TCE for mass calibration.

FIG. 2.9: The voltage divider for supplying the requisite power to the MCP.

FIG. 2.10: Flow chart of analysis procedure of REMPI data.

FIG. 3.1: REMPI-TOF profiles of Br(^2P_3/2) and Br*(^2P_1/2) produced from the 234 nm photodissociation of halothane. The circles are the experimental data and the solid line is a forward convolution fit.

FIG. 3.2: REMPI-TOF profiles of Cl(^2P_3/2) and Cl*(^2P_1/2) produced from the 234 nm photodissociation of halothane. The circles are the experimental data, the dashed lines are forward convolution fit for two different channels and the solid line shows the sum.

FIG. 3.3: Photofragment center-of-mass translational energy distribution for the 234 nm dissociation of halothane for Br elimination channel. The solid lines indicate the
translational energy distributions for the Br(\(^2P_{3/2}\)) and dotted line for Br\(^*\)(\(^2P_{1/2}\)) atom, respectively.

**FIG. 3.4:** Photofragment center-of-mass translational energy distribution of chlorine atom Cl(\(^2P_{3/2}\)) elimination channel for the 234 nm dissociation of halothane. The dashed lines indicate the energy distributions for the fast and slow component; the solid line shows the sum.

**FIG. 3.5:** Photofragment center-of-mass translational energy distribution of chlorine atom Cl\(^*\)(\(^2P_{1/2}\)) elimination channel for the 234 nm dissociation of halothane. The dashed lines indicate the energy distributions for the fast and slow component; the solid line shows the sum.

**FIG. 3.6:** REMPI profiles of Br and Br\(^*\) atoms produced in the 234 nm laser photolysis of halothane used for the determination of the spin-orbit ratio.

**FIG. 3.7:** REMPI profiles of Cl and Cl\(^*\) atoms produced in the 234 nm laser photolysis of halothane used for the determination of the spin-orbit ratio.

**FIG. 3.8:** The adiabatic potential energy curves of the four lowest states of halothane as a function of the C-Br bond length at the C-Cl bond lengths of 1.8, 2.0 and 2.2 Å.

**FIG. 4.1:** REMPI–TOF profiles of Cl (\(^2P_{3/2}\)) and Cl\(^*\) (\(^2P_{1/2}\)) produced from the photodissociation of tetrachloroethylene at 235 nm. The circles are the experimental data, the dashed lines are forward convolution fit for two different channels and the solid red curve shows the sum.
FIG. 4.2: Photofragment center-of-mass translational energy distribution of Cl(2P3/2) (black solid curve) and Cl*(blue dotted curve) elimination channel for the 235 nm dissociation of tetrachloroethylene.

FIG. 4.3: Computed HOMO, LUMO, along with other MOs involved in the transition of vinyl chloride, trichloroethylene and tetrachloroethylene.

FIG. 4.4: Various diabatic PESs calculated for vinyl chloride along the C–Cl bond.

FIG. 4.5: Various diabatic PESs calculated for (A) Trichloroethylene and (B) Tetrachloroethylene along the C–Cl bond.

FIG. 4.6: The diabatic PESs for the [π, σ*(C-Cl)] state involved in vinyl chloride, trichloroethylene and tetrachloroethylene.

FIG. 5.1: Time-of-flight mass spectra on photodissociation of 2-furoyl chloride on the Cl resonant line.

FIG. 5.2: REMPI-TOF profiles of Cl(2P3/2) and Cl*(2P1/2) produced from the 235 nm photodissociation of 2-furoyl chloride. The circles are the experimental data, dotted lines are two velocity components and the solid line is a forward convolution fit.

FIG. 5.3: Center-of-mass recoil translational energy distribution for Cl(2P3/2) in the photodissociation of 2-furoyl chloride at 235 nm. The dashed lines indicate the distributions for the slow and fast components of the chlorine atom formation channel; the solid line shows the sum.

FIG. 5.4: Center-of-mass recoil translational energy distribution for Cl*(2P1/2) in the photodissociation of 2-furoyl chloride at 235 nm. The dashed lines indicate the
distributions for the slow and fast components of the chlorine atom formation channel; the solid line shows the sum.

**FIG. 5.5:** REMPI spectra of Cl and Cl* atoms produced in the 235 nm laser photolysis of 2-furoyl chloride.

**FIG. 5.6:** The optimized structures of the ground (first, showing two conformers with corresponding TS, and third, depicting TS for CO elimination, rows) and excited electronic (second row, showing S₁, TS for Cl formation from S₁, and S₂ states) states of 2-furoyl chloride, along with transition states. Details are given in the text. A few important bond lengths (in Å) and dihedral angles are marked on structures. Dissociating and forming bonds are depicted as dotted lines.

**FIG. 5.7:** Relative potential energy diagrams for formation of Cl from the excited electronic state (S₁), and that of CO from the ground state of 2-furoyl chloride. Details are given in the text. All the energies are in kcal/mol.

**FIG. 5.8:** (2+1) REMPI spectra of H^{35}Cl (stronger line of the doublets) and H^{37}Cl (weaker line of the doublets), for the Q(J) branch of V \( ^1\Sigma^+ \) (0⁺)←← X \( ^1\Sigma^+ \) (0⁺) (12,0) band, produced in the 235 nm laser photolysis of benzoyl chloride. The line marked with an asterisk (*) stands for a Cl line.

**FIG. 5.9:** REMPI-TOF profiles of Cl(\( ^2\)P\( _{3/2} \)) and Cl*(\( ^2\)P\( _{1/2} \)) produced from the 235 nm photodissociation of benzoyl chloride. The circles are the experimental data, dotted lines are two velocity components and the solid line is a forward convolution fit.

**FIG. 5.10:** Center-of-mass recoil translational energy distribution for Cl(\( ^2\)P\( _{3/2} \)) in the photodissociation of benzoyl chloride at 235 nm. The dashed lines indicate the
distributions for the slow and fast components of the chlorine atom formation channel; the solid line shows the sum.

**FIG. 5.11:** Center-of-mass recoil translational energy distribution for Cl*(\(^{2}\text{P}_{1/2}\)) in the photodissociation of benzoyl chloride at 235 nm. The dashed lines indicate the distributions for the slow and fast components of the chlorine atom formation channel; the solid line shows the sum.

**FIG. 5.12:** REMPI spectra of Cl and Cl* atoms produced in the 235 nm laser photolysis of benzoyl chloride.

**FIG. 5.13:** The optimized structures of the ground state (S\(_0\)), excited electronic states (S\(_1\) and S\(_2\)) and TS (S\(_1\)-TS) for Cl formation from the S\(_1\) state of benzoyl chloride. Details are given in the text. A few important bond lengths (in Å) and angles are marked on structures. Dissociating and forming bonds are depicted as dotted lines.

**FIG. 5.14:** Gas phase UV absorption spectra of 2-furoyl chloride (0.6 Torr) recorded at room temperature.

**FIG. 5.15:** The optimized structures of all the molecular structures, including TS, produced during formation of HCl from the ground electronic states of benzoyl and 2-furoyl chlorides. Details are given in the text. A few important bond lengths (in Å) are marked on structures. Dissociating and forming bonds are depicted as dotted lines.

**FIG. 5.16:** Relative potential energy diagrams for formation of HCl from the ground electronic state (S\(_0\)) of benzoyl chloride (solid line) and 2-furoyl chloride (dotted line). Energies in parentheses pertain to 2-furoyl chloride, and all the energies are in
kcal/mol. Three different HCl pathways are depicted as A, B and C. Details are given in the text.

**Fig. 6.1:** LIF excitation spectrum of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ system of the nascent OH product from photodissociation of BNP (50 mTorr) at 193 nm.

**FIG. 6.2:** Boltzmann plots of rotational state population against energy of rotational states of OH ($v''= 0$) generated in dissociation of BNP at 248 and 193 nm.

**FIG. 6.3:** Doppler profiles of $P_1(5)$ line of the $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) system of the OH radical produced in dissociation of BNP at 248 and 193 nm.

**FIG. 6.4:** Plots of $\Lambda$-doublet (left y-axis, points marked as solid squares) and the spin-orbit state population ratio (right y-axis, points marked as open circles) against rotational quantum number $N''$ for the nascent OH formed in laser-induced photodissociation of BNP at 248 nm (upper plot) and 193 nm (lower plot).

**FIG. 6.5:** The dispersed fluorescence spectrum at 150 ns time delay from the pump laser pulse with a broad peak at ~540 nm, resulting from the photoexcitation of BNP at 193 nm.

**FIG. 6.6:** A typical observed fluorescence temporal profile (experimental points shown as open circles) at 540 nm after irradiation of BNP (175 mTorr) at 193 nm with a single-exponential fit (solid line) of its decay. The plot in the inset depicts the linear dependence of the fluorescence decay rates on varied pressures of BNP.

**FIG. 6.7:** Corrected REMPI spectral profiles of Br* and Br atoms produced in the 234 nm laser photolysis of BNP used for the determination of their spin-orbit ratio.
**FIG. 6.8:** REMPI-TOF profiles of Br($^2P_{3/2}$) and Br*(2P$_{1/2}$) produced from the 234 nm photodissociation of BNP. The circles are the experimental data and the solid line is a forward convolution fit.

**Fig. 6.9:** Photofragment translational energy distribution of Br($^2P_{3/2}$) and Br*(2P$_{1/2}$) for the 234 nm dissociation of BNP.

**FIG. 6.10:** The optimized structures of the ground electronic state of BNP and transition states of probable reactions producing OH. Details are given in the text. All structures are optimized at the B3LYP/6-311+G(d,p) level of theory. Dissociating bonds are depicted as dotted lines. Each TS structure is marked as TS-n, where n represents the reaction number (6.n).

**Fig. 6.11:** Relative potential energy diagrams for formation of OH from the ground electronic state of BNP. All energies (in kcal/mol) are at MP2/6-311+G(d,p) level of theory. Each TS is marked as TS-n, where n represents the reaction number (6.n). A number n in parenthesis also stands for a reaction (6.n). The curves in bold, dashed-dot and dot represent mechanism for OH formation at 193 nm, 248 nm and through nitrite form of BNP, respectively. The dashed curves represent a possible NO$_2$ formation channel.

**Fig. 6.12:** Relative potential energy diagrams for formation of Br from the ground electronic state of BNP. All energies (in kcal/mol) are at MP2/6-311+G(d,p) level of theory. Each TS is marked as TS-n, where n represents the reaction number (6.n). A number n in parenthesis also stands for the corresponding reaction (6.n).
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