
Monali Kawade, Ankur Saha, Hari P. Upadhyaya,* Awadhesh Kumar, Prakash D. Naik, and P.N. Bajaj

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

ABSTRACT: The photodissociation dynamics of fumaryl chloride (CICO—CH=CH—COCl) has been studied in a supersonic molecular beam around 235 nm using resonance enhanced multiphoton ionization (REMPI) time-of-flight (TOF) technique by detecting the nascent state of the primary chlorine atom. A single laser has been used for excitation of fumaryl chloride and the REMPI detection of chlorine atoms in their spin–orbit states, Cl (2P3/2) and Cl* (2P1/2). We have determined the translational energy distribution, the recoil anisotropy parameter, β, and the spin–orbit branching ratio for chlorine atom elimination channels. To obtain these, measured polarization-dependent and state-specific TOF profiles are converted into kinetic energy distributions, using a least-squares fitting method, taking into account the fragment recoil anisotropies, β. The TOF profiles for both Cl and Cl* are found to be independent of laser polarization; i.e., β is well characterized by a value of 0.0, within the experimental uncertainties. Two components, namely, the fast and the slow, are observed in the translational energy distribution, P(Et), of Cl and Cl* atoms, and assigned to be formed from different potential energy surfaces. The average translational energies for the fast components of the Cl and Cl* channels are 14.9 ± 1.6 and 16.8 ± 1.6 kcal/mol, respectively. Similarly, for the slow components, the average translational energies of the Cl and Cl* channels are 3.4 ± 0.8 and 3.1 ± 0.8 kcal/mol, respectively. The energy partitioning into the translational modes is interpreted with the help of various models, such as impulsive and statistical models. Apart from the chlorine atom elimination channel, molecular hydrogen chloride (HCl) elimination is also observed in the photodissociation process. The HCl product has been detected, using a REMPI scheme in the region of 236–237 nm. The observation of the molecular HCl in the dissociation process highlights the importance of the relaxation process, in which the initially excited parent molecule relaxes to the ground state from where the molecular (HCl) elimination takes place.

I. INTRODUCTION

Photodissociation dynamics of carbonyl compounds always has been an area of extensive research that has been pursued with both experimental and theoretical approaches. The existence of close-lying excited states and their interactions is mainly a great attraction for the researchers. Again, the compounds with two carbonyl groups (diketones), provide useful information for the study of intramolecular energy transfer, and interactions involving remote carbonyl groups. It is very interesting to study and identify the mechanism of these types of interactions between the carbonyl groups. Besides these diketones, there is another class of compounds, generally termed as α,β-enones, in which the carbon–carbon double bond (–C==C–) is in conjugation with carbonyl group (–C=O) giving rise to altogether a different and interesting photochemistry. These α,β-enones undergo a variety of photochemical rearrangements and their photochemistry, in general, has attracted much attention in recent years. In our earlier studies, we investigated the dynamics of formation of the OH radical in photodissociation of few enones, such as acrylonitrile (H2C=CHCN), propionitrile (CH3CH2CN), acrylonitrile (H2C=CHCN), propionitrile (CH3CH2CN), and pyruvic acid [CH3COCOOH]5 using laser photolysis-laser induced fluorescence (LP-LIF) technique.

Numerous studies on the photodissociation of carbonyl chlorides are available in the literature; very few of these are focused on the photochemistry of fumaryl chloride. The UV photodissociation of the most elementary acid chlorides, acetyl chloride (CH3COCl), and propionyl chloride (CH3CH2COCl), have been previously studied in both gas and solid phases. Acetyl chloride on photodissociation at 236 nm produces acetyl and chlorine radicals while propionyl chloride gives ketene (H2C==C==O) and HCl as well. Photodissociation and isomerization processes of acryloyl chloride (CH2==CHCOCI), an enone similar to fumaryl chloride, have been studied both experimentally and theoretically.11 Apart from the Cl atom formation channel, it photodissociates through two additional channels, one produces ketene and HCl (same as in propionyl chloride), while the other channel involves a 1,3-sigmatropic rearrangement, producing 3-chloro-1,2-propenone (H2C=ClCCH==O). Extensive UV

Received: October 20, 2010
Revised: January 12, 2011
Published: February 15, 2011
photodissociation studies of oxalyl chloride, (ClCO)$_2$, a lower homologue of fumaryl chloride, have been carried out. Suits and co-workers investigated photodissociation dynamics of oxalyl chloride near 235 and at 193 nm, with a photofragment imaging technique, using REMPI detection of Cl and CO moieties. They suggested that the photodissociation of (ClCO)$_2$ proceeds via an impulsive three-body mechanism yielding translationally hot spin−orbit excited Cl* and ground state Cl, together with translationally hot and rotationally excited CO, and a translationally cold ClICO. The primary product COCl undergoes subsequent dissociation to yield slow CO and Cl. They also measured the translational energy distribution and anisotropies of Cl, Cl*, and CO.

Fumaryl chloride, as shown in Figure 1, is a planar molecule and has three stable isomers, out of which two isomers, namely, trans−trans and cis−cis, belong to the $C_{2h}$ point group and the third trans−cis isomer belongs to the $C_1$ point group. The relative abundances of these isomers are found to be 30%, 24%, and 46%, respectively, at 480 K. A negligible effect of temperature on the relative abundance indicates only small energy differences among the isomers. The complete IR and Raman studies of liquid and crystal forms have identified two conformers as trans−trans and cis−trans. It has a symmetric structure with both carbonyl groups associated with an identical functionality.

The thermal decomposition of fumaryl chloride at 900 °C gives rise to various products, such as C$_3$O(C=O)HCl, and CO. Besides, fumaryl chloride has many synthetic applications, mainly because it contains unsaturated carbon−carbon double bonds, which can be used for in situ cross-linking. Jabbari et al. have suggested that it can be copolymerized with a poly(e-caprolactone) for constructing a biocompatible, bioresorbable, injectable, and self-cross-linkable polymer for bone tissue engineering. Poly(ethylene glycol) fumarate, synthesized from fumaryl chloride and polyethylene glycol in the presence of propylene glycol, is used as a rigid coating for the superparamagnetic iron oxide nanoparticles, which are increasingly being evaluated for clinical applications such as hyperthermia, drug delivery, magnetic resonance imaging, transfection, and cell/protein separation. Several ultrastructure cross-linked and functional polymer thin films, for potential nonlinear optical (NLO) application, or other applications requiring molecular orientation, are synthesized from fumaryl chloride and maleic anhydride.

The present study is undertaken to understand the photodissociation dynamics of fumaryl chloride (ClCO−CH=CH−COCl), a molecule with two C=O groups and a C=C group in conjugation, in a supersonic molecular beam around 235 nm. The chloride atom product in both the ground state ($^3P_{3/2}$) and the spin−orbit excited state ($^3P_{1/2}$) has been detected using the REMPI-TOF technique. We have also measured the translational energy distributions for both types of chlorine atoms and relative quantum yield of Cl*. To gain further insights, the anisotropy parameters ($\beta_\perp$) were also measured.

II. EXPERIMENTAL SECTION

The experiment was performed, using a molecular beam time-of-flight mass spectrometer system (MB-TOF-MS), as described in our earlier studies on photodissociation of PCl$_3$. Briefly, it consists of a supersonic beam source and an ionization (beam−laser interaction) region, which were differentially pumped, using turbomolecular pumps (TMP), backed by rotary pumps. An additional 4 in. TMP was used to pump the TOF tube and mounted near the detector. Typical operating pressures in the source and the ionization regions were $5 \times 10^{-7}$ and $8 \times 10^{-7}$ Torr, respectively. A pulsed supersonic free jet was generated, using a solenoid valve. The free jet was skimmed off by a 1.9 mm diameter conical skimmer generating a supersonic molecular beam (MB), which was directed to the interaction region. The pulsed valve was located ~2 cm from the skimmer, and 7.5 cm from the interaction region. The MB pulse profile and the number density were characterized, using a fast ion gauge (FIG), located beyond the ion optics. The fumaryl chloride sample (95% purity, Aldrich) was used, without further purification. Helium was bubbled through the sample maintained at room temperature, and the mixture was expanded through the nozzle at a stagnation pressure of 1000 Torr of He. It was ensured that any interference to the measurements due to cluster photofragmentation was absent by operating at a low stagnation pressure, and using only the rising part of the molecular beam pulse.

The detector system consists of a two-stage Wiley−McLaren time-of-flight mass spectrometer (TOF-MS), with extraction and acceleration regions. The system is mounted vertically, perpendicular to the horizontal MB. The extraction region consists of a repeller electrode and an extractor grid, mounted 10 mm above the repeller electrode. The acceleration region is defined by the extractor electrode and a grid held at the ground potential, separated from each other by 10 mm. Both these grids (5 cm × 5 cm) are constructed from stainless steel mesh, with 90% transmission. To collect the total ions, the extraction region was held at ~300 V/cm, and the acceleration region was held at ~3900 V/cm. After passing through the acceleration region, the ion packet passed through a 1035 mm long field-free flight tube to the detector. Two deflector plates, placed perpendicular to the detector axis (z axis), allowed the ion packet to be translated in the (x, y) plane, to center it on the detector. The typical field strength for the deflector plates was 2−6 V/cm. The ions were detected by a set of 18 mm dual microchannel plates (MCP). A single compact voltage generator, having multiple output voltage ports, was employed to power the TOF ion optics, the deflection plates and the MCP detector.

The chlorine atoms were probed, using 2 + 1 resonance enhanced multiphoton ionization (REMPI) transitions in the region 234−236 nm. The laser pulses were generated by a dye laser (TDL 90, Quantel), using rhodamine 101 dye. The dye laser was pumped by 332 nm light from the second harmonic of a Nd:YAG laser (YG-981-C, Quantel), operating at 20 Hz. The fundamental dye laser output was frequency-doubled in a KDP crystal, and mixed with the fundamental output of the Nd:YAG laser, to obtain an output in the range 230−236 nm. In all the experiments reported in this work, the same laser beam was employed as a pump as well as a probe, i.e., for both photodissociation of the parent molecule and ionization of the photoproducts, Cl($^3P_{3/2}$) and Cl*($^3P_{1/2}$) atoms. The laser beam was focused by a lens of...
200 mm focal length, and the distance of the lens from the center of the molecular beam axis was varied, to obtain the best ratio of on- and off-resonant signals. The spin–orbit ratio was determined from the ion intensities for the corresponding transitions, after correction due to their two-photon oscillator strengths. For this purpose, two lines were chosen, one at 42492.2 cm⁻¹ and another at 42516.1 cm⁻¹, corresponding to 4p ¹D₁/₂ → 3p ¹P₃/₂ and 4p ¹P₁/₂ → 3p ¹P₃/₂ transitions, respectively. The polarization of the resultant laser beam was rotated, using a double Fresnel rhomb, and a polarizer ensured 99% polarization of the laser beam entering the chamber. The laser power was monitored, using a power meter, and was typically 50–100 µJ/pulse. To obtain the TOF mass spectrum, the signal was sent to a digital oscilloscope, which was interfaced to a PC. Subtracting the off-resonant signals from the on-resonant signals effectively removed the minor pump-oil related background contribution to the TOF spectra, and also the contribution from a multiphotonic process. A digital delay/pulse generator, with pulse resolution of 20 ps, was employed as the master to trigger all the instruments for time synchronization. The time delay between the trigger pulse applied to the pulsed valve and its opening was obtained by measuring the delay between the trigger pulse and the fast ionization gauge (FIG) signal, employing a digital oscilloscope. This delay is the sum of the time required to open the pulsed valve from its trigger input and that for the molecular pulse to reach FIG from its position of generation, i.e., the nozzle exit. By measuring these time delays for different FIG positions with respect to the skimmer, we estimated the flow velocity of the molecular beam and used it to obtain the time required for the molecular beam to reach the extraction region of the TOFMS. A PC was used to control the scan of the dye laser via an RS232 interface, and collect data from SRS 245, through a GPIB interface, using a control and data acquisition program. The power dependence measurements were performed by integrating the chlorine atom REMPI spectra, which were obtained by sending the detector output directly to a boxcar integrator, gated on the m/z 35 and m/z 37 peaks in the TOF mass spectrum. The laser power was varied, and the boxcar output was recorded at each power. The REMPI spectra and survey scans were taken by recording the boxcar output as a function of the laser wavelength and archiving the spectra on a PC interfaced to the dye laser controller. TOF profiles were taken for three different experimental configurations, vertical (laser polarization II detection axis), horizontal (laser polarization ⊥ detection axis), and magic angle (laser polarization at 54.7° to detection axis). Doppler broadening of the transitions was always well within the laser bandwidth. For polarization experiments, TOF profiles were averaged for a minimum of 10000 laser shots.

III. RESULTS AND ANALYSIS

A. Analysis. We have measured TOF profiles of Cl and Cl⁺ at different laser polarizations. The translational energy distribution and the anisotropy parameter for both Cl and Cl⁺ are determined from these TOF profiles, using a commonly used forward convolution (FC) technique, as described in our earlier publication. In this method, the knowledge of the instrumental response function is required, and the same is determined by studying the REMPI of aniline beam. The REMPI spectrum of aniline recorded at 34029 cm⁻¹ (293.77 nm) matches very well with that reported in the literature. The aniline molecular ion signal was measured as a function of laser intensity, at the resonance wavelength, and found to be quadratic dependent. This shows that, at 293.77 nm, the REMPI is 1 + 1 type because of one photon resonant transition, ¹A₁ → ¹B₂, followed by pumping to the ionization continuum by absorption of a second photon. Such measurement showed the instrumental response function to be well described by a fixed 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 Vₑ.

The forward convolution method that we have employed has been discussed in our previous publication and will be only briefly outlined. In the REMPI-TOF-MS technique, the component of the photofragment that speeds along the TOF-MS axis, which defines the lab frame Z axis, is measured. This speed component results from the averaging of the angular distribution, as described, over the photofragment speed distribution, g(v), and is given as

\[ f(v, χ) = \int_{[v]}^{\infty} \frac{g(v)}{2v} \left( 1 + \beta P_2(\cos \chi) P_2 \left( \frac{v_z}{v} \right) \right) dv \]  

where \( v_z \) is the velocity component along the Z axis, v is the recoil speed of the fragments, and \( \beta \) is the anisotropy parameter given by \( \beta = 2\langle P_2(\cos \theta) \rangle \). \( \theta_m \) is the molecular frame angle between the molecular transition dipole moment and the photofragment recoil direction, \( P_2(\cos \chi) \) is the second-order Legendre polynomial, and \( \cos(\chi) = \hat{e} \cdot \hat{z} \) in the above equation is the projection of the pump laser electric field, \( \hat{e} \), on the detector axis, \( \hat{z} \), which is also defined as the angle between the dissociation laser polarization and the Z axis. In the present work, we have used a procedure of noncore sampling data, in which it is assumed that the nature and the shape of the TOF profiles for chlorine photofragment is independent of the probe polarization. In general, this assumption holds good. But, the presence of atomic v·j correlation might make this assumption only approximate. However, these correlations are weak enough to be neglected. In the case of several contributing channels, eq 1 must be summed over the photofragment speed distribution, \( g(v) \), and anisotropy, \( \beta \), of each channel. The dependence of \( f(v, χ) \) on \( \beta \) can be eliminated by either measuring the data with the magic angle of \( χ = 54.7° \), where \( P_2(\cos \chi) = 0 \), or coadding normalized profiles with \( χ = 90° \) and \( χ = 0° \), giving a 2:1 weightage. Both the approaches yield isotropic \( f(v, χ) \) profiles, and the total center of mass (c.m.) speed distribution is obtained by differentiation of eq 1 at \( χ = 54.7° \) and is given as

\[ g(v) = -2v \frac{d}{dv} f(v, 54.7°) \]

The measurements in this work were recorded as TOF spectra, i.e., in the time domain \( I(\chi) \). Under space focusing conditions, a simple linear transformation gives the signal in the velocity domain, \( I(v, χ) \), according to,\( v_z = (qVₑ/(1-t_0))/m \), where \( q \) and \( m \) are the charge and mass of the photofragment, respectively, \( Vₑ \) is the electric field in the extraction region, and \( t_0 \) is the mean time-of-flight. Application of eq 1 on the magic angle TOF profile \( I(v, 54.7°) \) yields an estimate of the total c.m. speed distribution \( g(v) \) and, in turn, some indication of the form of the individual speed distributions \( g(v) \). These are usually modeled with the functional form

\[ g(v) = (f_T) a (1 - (f_T)) b \]

where \( f_T \) is the fraction of the available energy channeled into translational modes, \( E^{\text{trans}}/E^{\text{total}} \), and \( a \) and \( b \) are adjustable.
parameters. By taking into account an adjustable anisotropy parameter $\beta$, and weight for each decay channel, we simultaneously calculate $f(v_{2P_1/2})$ for the geometries $\chi = 0^\circ$, 54.7$^\circ$, and 90$^\circ$. Convolution with the instrument response function yields simulated TOF profiles, which can be compared with the experimental results. The parameters are then adjusted until a satisfactory agreement with the experimental data is achieved. Once the photofragment speed distributions have been determined, these may be used to obtain the corresponding translational energy distributions.

Figure 2 shows the power dependence of the one-color REMPI signals for transitions corresponding to Cl ($^{2}P_{3/2}$). The signal is linear in a log–log plot over the range of powers used in the present study. For both the types of chlorine atoms, the lines exhibit a slope of $\sim 3.1 \pm 0.2$, which is consistent with one-photon dissociation of fumaryl chloride, followed by $2 + 1$ REMPI of the chlorine atoms, assuming that the ionization step is saturated. Apart from the power dependence studies, we also systematically monitored the shape and the width of TOF profiles of Cl atoms at various laser intensities. All the experiments were performed in the intensities, which are much lower than the intensity at which the shape and width of the TOF profiles were invariant. This experimental condition ensures that the translational energy distributions and the anisotropy parameters are invariant over the laser fluences used.

B. Spin–Orbit Branching Ratio. Figure 3 shows typical Doppler profiles of Cl ($^{2}P_{3/2}$) and Cl* ($^{2}P_{1/2}$) atoms produced in the dissociation of fumaryl chloride on excitation at 235 nm, which are wavelength scans in the region 235.336 and 235.205 nm, respectively. The relative quantum yield of chlorine atom fragments in different spin–orbit states was determined by normalizing the integrated intensity, i.e., peak areas, $S$(Cl) or $S$(Cl*), of the respective $2 + 1$ REMPI transitions with respect to the laser intensity, and the ratio of the two-photon absorption coefficients. The measured area of $2 + 1$ REMPI lines is proportional to the actual product ratio, with a factor of $k_*$, which is the relative ionization probability for Cl and Cl*, $f$(Cl)/$f$(Cl*),

$$N$(Cl*)

$$ = k_S$(Cl*)/$S$(Cl)

where $N$(Cl) and $N$(Cl*) designate the number density of Cl and Cl* produced. $S$(Cl) and $S$(Cl*) are obtained by integrating the measured ion signal intensity over the proper range containing the Doppler width and the probe laser bandwidth. The measurements were repeated at different laser light intensities, giving similar relative signal intensities. For fumaryl chloride photodissociation, the ion integrated signal intensity ratio, $S$(Cl*)/$S$(Cl), has been measured to be 0.39 ± 0.06. From the measured integrated intensity ratio, one can easily obtain the product ratio, using the above eq 4, by taking a value of 0.85 ± 0.10 for $k_*$.

The relative quantum yields, $\Phi$(Cl) and $\Phi$(Cl*), can be determined from the product ratio, and $\Phi$(Cl*) can be expressed as

$$\Phi$(Cl*)

$$ = \frac{N$(Cl*)}{N$(Cl) + N$(Cl*)}

The value of $\Phi$(Cl*) calculated for fumaryl chloride dissociation is found to be 0.24 ± 0.03. On statistical grounds one expects a quantum yield, $\Phi$(Cl*) = 0.33. As described in the later section, the low quantum yield for the Cl* can be attributed to the fact that the C=C bond fission via the lowest-recoil-kinetic energy mechanism mainly produces Cl atoms in the Cl* ($^{2}P_{1/2}$) state; the same is true for the lowest-kinetic-energy C=Cl bond fission channel in photodissociation of many other alkyl chlorides.

C. Translational Energy Distribution and Anisotropy Parameter. The measured Cl atom TOF profiles were analyzed to determine the kinetic energy distribution and average kinetic energy of the fragments in the fumaryl chloride photodissociation at $\sim 235$ nm. The TOF profiles for the Cl and Cl* atoms were converted to the velocity domain. Figures 4 and 5 show background subtracted TOF spectra, recorded for the laser polarization parallel, at the magic angle $\sim 54.78^\circ$ and perpendicular to the detection axis, for the Cl and Cl* fragments, respectively. We analyzed the TOF data, using a forward convolution procedure, as described in the earlier section. Here, an initial photofragment speed distribution, $g(v)$, and the anisotropy parameter $\beta$ are assumed. As atomic v·j correlations are known to be very weak, we can safely assume the TOF profiles to be independent of the probe polarization. The TOF profiles are calculated for the three experimental configurations, convoluted with the instrumental response function determined, as described in an earlier section, and are compared with the experimental results. The translational energy distributions, $P(E_T)$, determined from the data in Figures 4 and 5, for the Cl and Cl*, are depicted in Figures 6 and 7. Inspection of Figures 6 and 7 reveals that the $P(E_T)$ consists of two components. For the Cl and Cl*
atom, the faster component, centered at $\sim 14.4$ kcal/mol, consists of 67 ± 5% of the total fragments while the slower component, centered at $\sim 2.7$ kcal/mol, consists of the remaining 33 ± 5%. Similarly, for Cl*, the faster component, centered at $\sim 16.8$ kcal/mol, consists of 87 ± 5% of the total fragments while the slower component, centered at $\sim 2.4$ kcal/mol, consists of the remaining 13 ± 5%. It was not possible to determine independently the anisotropy parameter for the two components, and hence, the anisotropies were assumed to be identical for each channel. The TOF profiles for both Cl and Cl* are independent of laser polarizations, implying the $\beta$ is well characterized by a value of $\sim 0.0$, within the experimental uncertainties. The calculated TOF profiles are displayed by the solid line, with each component shown by a dotted curve. The difference in the TOF profile for Cl and Cl* in Figure 4 and 5 arises mainly due to the different nature of $f_T$, their nonstatistical branching ratio and the ratio of fast to slow component.

**D. HCl Formation Channel.** The multiphoton ionization spectrum of fumaryl chloride at 235 nm clearly shows peaks at $m/e$ 36 and 38, corresponding to H$^{35}$Cl and H$^{37}$Cl, respectively. To explore the origin of the HCl mass peak, the laser wavelength was scanned over its REMPI region in the range 236–237 nm. In our experiments, we did find 2+1 REMPI lines of HCl in the TOF spectra in the range 236–237 nm, for the Q(J) branch of the V $^1 \Sigma^+$ (0 $^+$) $\rightarrow$ X $^1 \Sigma^+$ (0 $^+$) (12,0) band system. Although the signal was weak due to the predissociative nature of this particular transition, we were able to carry out the power dependence studies. The predissociative nature of this transition was also established in our experiment, since we observed the corresponding Cl and H atom ion signals at the

![Figure 4](image1.png)  
**Figure 4.** REMPI-TOF profiles of Cl($^2P_{3/2}$) produced from the 235 nm photodissociation of fumaryl chloride. The circles are the experimental data and the solid line is a forward convolution fit. Three panels, namely, upper, middle, and lower panels, correspond to horizontal, magic angle, and vertical experimental geometries, respectively.

![Figure 5](image2.png)  
**Figure 5.** REMPI-TOF profiles of Cl($^2P_{1/2}$) produced from the 235 nm photodissociation of fumaryl chloride. The circles are the experimental data and the solid line is a forward convolution fit. Three panels, namely, upper, middle, and lower panels, correspond to horizontal, magic angle, and vertical experimental geometries, respectively.

![Figure 6](image3.png)  
**Figure 6.** Center-of-mass recoil translational energy distribution derived from Figure 4 for Cl($^2P_{3/2}$) in the photodissociation of fumaryl chloride at 235 nm. The dashed lines indicate the speed distributions for the fast and slow components of the chlorine atom formation channel; the solid line shows the sum. The vertical arrow indicates the maximum available energy for Cl($^2P_{3/2}$) elimination channel.

resonant wavelength corresponding to the REMPI lines of HCl molecules. A linear log–log plot for the power dependence studies shows a slope of $\sim 2.9 \pm 0.2$, which is consistent with one-photon dissociation of fumaryl chloride forming HCl followed by
its detection with the 2+1 REMPI scheme, similar to the dynamics of Cl atom formation. Laser polarization dependent studies on the HCl TOF profile to elucidate the translational energy distribution could not be done due to weak signal, as discussed earlier. The above set of experiments establishes the formation of HCl in the photodissociation of fumaryl chloride at 235 nm as a primary channel.

IV. DISCUSSION

A. Nature of Excitation at 235 nm. As discussed earlier, fumaryl chloride contains one C=C— and two C==O groups in conjugation, which make it bichromophoric, similar to fumaric acid (HOCO—CH==CH—COOH) and acryloyl chloride (H₂C==CHCOCl). Hence, we expect that fumaryl chloride also has a similar type of absorption spectrum with two bands corresponding to n—π* and π—π* transitions. Ab initio molecular orbital (MO) calculations were performed to investigate the nature of the excited electronic states of fumaryl chloride. We optimized ground state geometries of various isomers, as shown in Figure 1, employing time dependent (TD) density function theory (DFT) calculation, using the cc-pVdz set of basis sets. There are three isomers, namely, cis—cis, cis—trans, and trans—trans, for fumaryl chloride. Theoretical calculations predict that the relative stabilities of all three isomers differ by less than 0.5 kcal/mol. Thus, these isomers are indistinguishable, given the experimental uncertainty of present study and the accuracy of the theoretical methods employed here. Vertical excitation energies were obtained for various transitions, to understand the nature of excitation at 235 nm. Although the calculated vertical transition energies are red-shifted compared to the experimental results in case of fumaric acid, the nature of transition and the orbitals are accurately predicted using this method. Orbitals participating in the different electronic transitions were visualized for better understanding of the process. The vertical excitation of fumaryl chloride is associated with a strong π—π* transition at higher energy and a weaker n—π* at lower energy. The strong transition, with oscillator strengths exceeding 0.4, is the first π—π* transition and is termed as S₂. Topological analyses of the electron density notably highlight the delocalized nature of the O==C—C==C—C==O chain, whereby the central C==C bond possesses the largest electron density, although less than the pure π-bonds. The C—C bonds consequently possess larger electron populations than the expected σ-bonds. The nature of π and π* orbitals in this transition is having a mixed character involving mainly the C==C and the C==O π electrons. The weaker n—π* transitions at lower energy is termed as S₁ and it mainly involves the transition from the nonbonding orbitals of both Cl and O to the π* orbitals, which have a mixed character as discussed earlier. At 235 nm, we believe that fumaryl chloride is excited to the S₂ state. This S₂ state adiabatically correlates only with highly excited photoproducts, and that is not feasible in a single-photon excitation in the present case. Therefore, it is assumed that fumaryl chloride from the S₂ states crosses over to the nearby states, mostly the n—σ* state, from where the C—Cl bond cleaves forming Cl atoms. Also, it can undergo rapid internal conversion to the ground state, from where various other dissociation channels can occur, in addition to the Cl atom elimination.

B. Translational Energy Release and Anisotropy Parameter. Several processes have been proposed as primary dissociation pathways in fumaryl chloride photoexcitation at 235 nm, and these are given as follows:

\[
\text{ClOCH}=\text{CH}=\text{CH}=\text{COCl} \rightarrow \text{ClOCH}=\text{CH}=\text{CH}+\text{CO}+\text{Cl} \quad \Delta H = 83 \text{ kcal/mol} \quad (6)
\]

\[
\rightarrow \text{ClOCH}=\text{CH}=\text{CH}+\text{COCl} \quad \Delta H = 100 \text{ kcal/mol} \quad (7)
\]

\[
\rightarrow \text{ClOCH}=\text{CH}=\text{CH}+\text{HCl} \quad \Delta H = 38 \text{ kcal/mol} \quad (8)
\]

Reactions 6 and 7 involve the cleavage of single bonds C—Cl and C—C, respectively, while reaction 8 is the HCl molecular elimination channel. The Cl atom can be produced directly from reaction 6 as a primary product and also from the subsequent dissociation of highly energetic COCl radical (reaction 9) formed in reaction 7 as a secondary product. The ΔH values are taken as similar to that of acryloyl chloride from refs 42 and 43.

\[
\text{COCl} \rightarrow \text{CO}+\text{Cl} \quad \Delta H = 8 \text{ kcal/mol} \quad (9)
\]

In fumaryl chloride, two types of \( P(E_T) \) were observed for the C—Cl fission: one producing fragments with high kinetic recoil energies and the other producing fragments with low recoil energies. The \( P(E_T) \) for Cl(2P$_{3/2}$) derived from the forward convolution fit to the high-translational energy C—Cl fission channel peaks near 14.4 kcal/mol and extends to 30.0 kcal/mol. Similarly, the low translational energy C—Cl bond fission channel peaks at 2.7 kcal/mol and extends to 10 kcal/mol. The presence of two types of \( P(E_T) \) in C—Cl bond fission is analogous to other systems involving a π—π* transition, such as acryloyl chloride,$^{43,44}$ allyl chloride,$^{45,46}$ and 2-chloropropane.$^{47}$ The high translational energy chlorine atom channel, most likely, arises from an electronic predissociation via a state repulsive in the C—Cl bond, as seen in the above systems. It is possible that the low translational energy channel results from the C—Cl fission following internal conversion to the ground electronic state. Another possibility of low energy Cl atom formation may arise from reaction 9. However, the formation of the COCl radical cannot

Figure 7. Center-of-mass recoil translational energy distribution derived from figure 5 for Cl(2P$_{3/2}$) in the photodissociation of fumaryl chloride at 235 nm. The dashed lines indicate the speed distributions for the fast and slow components of the chlorine atom formation channel; the solid line shows the sum. The vertical arrow indicates the maximum available energy for Cl(2P$_{3/2}$) elimination channel.
compete with the Cl formation channel due to its high endothermicity on the ground potential energy surface. So the only possible route for the formation of COCl, and hence, formation of Cl from it, is from a higher excited state such as, S\textsubscript{1}, T\textsubscript{2}, and T\textsubscript{1}. But this route for the COCl formation is also ruled out in acryloyl chloride, a molecule with photochemical behavior similar to that of fumaryl chloride, on the basis of theoretical studies by Cui et al.\textsuperscript{11} The nature of P(E\textsubscript{T}) of the slow Cl atom obtained in the present studies for fumaryl chloride also rules out this route on the basis of energy consideration. So, the only formation pathway for the slow Cl atom is attributed to the dissociation process from the ground electronic state, after internal conversion. This proposition is further supported by the fact that we did observe the molecular HCl elimination channel, which is conclusively from the ground state of fumaryl chloride.

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. Very often, the disposition of the available energy into the fragment translational and the internal degrees of freedom can be predicted, using simple models. These models generally fall into two categories: impulsive and statistical. It is well-known that the energy partitioning for a dissociative event on a repulsive surface is well described by an impulsive model. So, an impulsive model\textsuperscript{24,48,49} has been used in this case, to calculate theoretically the translational energy released to the products. 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 products. 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\textsubscript{avail}) released as translational energy is given by

\[ E_T = \left( \frac{\mu_{\text{Cl}-\text{Cl}}}{\mu_{\text{ClCOCHCHCO}}-\text{Cl}} \right) E_{\text{avail}}, \quad \text{and} \quad f_T = E_T / E_{\text{avail}} \]  

(10)

where \( \mu_{\text{Cl}-\text{Cl}} \) is the reduced mass of the C and Cl atoms, \( \mu_{\text{ClCOCHCHCO}}-\text{Cl} \) is the reduced mass of the ClCOCHCHCO and Cl, \( E_{\text{avail}} \) is the available energy, and \( f_T \) is the fraction of the available energy going into the translational modes of the fragments. In the case of fumaryl chloride, the ratio of reduced masses is 0.32. The available energy is given by

\[ E_{\text{avail}} = E_{\text{hv}} - D_0^\text{r} (\text{ClCOCHCHCO} - \text{Cl}) - E_{\text{SO}} \]  

(11)

where \( E_{\text{hv}} \) is the photon energy (122.0 kcal/mol), \( D_0^\text{r} (\text{ClCOCHCHCO} - \text{Cl}) \) is the C–Cl bond dissociation energy, and \( E_{\text{SO}} \) is the spin–orbit energy of chlorine (2.4 kcal/mol). The bond dissociation energy is taken as 83.0 kcal/mol, similar to that for acryloyl chloride.\textsuperscript{43} Thus, \( E_{\text{avail}} \) for the Cl and Cl\textsuperscript{*} channels are 39.0 and 36.6 kcal/mol, respectively. The experimental average translational energy (E\textsubscript{T}) for the fast component is found to be 14.9 ± 1.6 and 16.8 ± 1.6 kcal/mol for Cl and Cl\textsuperscript{*} channels, respectively, giving the \( f_T \) values of 0.38 and 0.46 for the Cl and Cl\textsuperscript{*}, respectively. The experimental determined \( f_T \) so obtained is slightly higher than the value of 0.32 predicted, using the impulsive model.

Now, coming to the slow component in the translational energy distribution of the Cl atom, the average energies determined are found to be 3.4 ± 0.8 and 3.1 ± 0.8 kcal/mol, for Cl and Cl\textsuperscript{*}, respectively. These values give the same \( f_T \) of 0.08, for both Cl and Cl\textsuperscript{*}, even though the available energies differ by 2.4 kcal/mol (spin–orbit energy) for these channels. A low \( f_T \) value suggests that the kinetic energy released for the slow component can be explained better in light of a statistical model. The statistical model assumes partitioning of the available energy democratically throughout the molecule and therefore neglects the effects of specific dynamical interactions of the departing fragments. A statistical dissociation process is predominant for a long-lived photoexcited parent molecule, allowing partitioning of the excess energy statistically among the available degrees of freedom of the products. This may be applicable in a process involving a rapid internal conversion to the ground electronic state, 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{50,51} were adopted, which give the \( f_T \) value of 0.07, matching very well with the experimental value of 0.08. This implies that the slow component in the translational energy distribution is mainly due to the Cl atom, which arises from the ground state potential energy surface, after internal conversion via some curve crossing mechanism. This mechanism is further confirmed by observation of the molecular HCl elimination channel, as described earlier.

The higher experimental \( f_T \) value as compared to that calculated using the impulsive model obtained in the dissociation of fumaryl chloride for the fast chlorine atom channel prompted us to apply the hybrid model, employed by North et al.\textsuperscript{52} for reactions with barrier. In this model, the \( E_{\text{avail}} \) for the products is divided into two parts, namely, the excess energy above the exit barrier (\( E_{\text{stat}} \)) and at the exit barrier energy (\( E_{\text{imp}} \)). The partitioning of \( E_{\text{stat}} \) and \( E_{\text{imp}} \) is treated by the statistical and modified impulsive models, respectively. The energy partitioned into each fragment is then obtained by adding contributions from each of these two models. For this type of dissociation with barrier, \( E_T \) does not change much with \( E_{\text{avail}} \). Similar results were obtained in our earlier studies on various saturated and unsaturated carboxylic acids, and also on the enone system.\textsuperscript{2,3} Photodissociation studies on acryloyl chloride by Butler and co-worker\textsuperscript{29,53} at 193 and 235 nm show similar translational energy release for the Cl atom. At 193 nm dissociation, \( E_T \) was obtained to be 27 kcal/mol. Similarly, at 235 nm dissociation, a value of 23 kcal/mol was obtained. Here, it can be clearly seen that the change in the \( E_{\text{avail}} \) from 65 kcal/mol (for 193 nm) to 39 kcal/mol (for 235 nm) did not change the \( E_T \) value considerably for the Cl atom dissociation channel in acryloyl chloride. Also, the theoretical calculation by Cui et al.\textsuperscript{11} clearly shows the presence of an exit barrier in the \( S_1(\pi^\text{a} \rightarrow \pi^\text{b}) \) state, for the Cl atom dissociation channel. So, we strongly believe that the dissociation from the \( S_1 \) state with an exit barrier cannot be ruled out in the photodissociation of acryloyl chloride in addition to dissociation from the repulsive state with \( (n^\text{a} \sigma^\text{a}) \) nature. With the same analogy, we propose that in fumaryl chloride the initially prepared \( S_2(\pi^\text{a} \rightarrow \pi^\text{b}) \) state crosses over to various states, namely, \( S_1(\pi^\text{a} \rightarrow \pi^\text{b}) \), \( (n^\text{a} \sigma^\text{a}) \), and the ground state. Finally, the Cl atom can be formed from all these states with different values of \( E_T \).

In the analysis of the recoil anisotropy, \( \beta \), for the Cl fragment, we note that in the limit of an instantaneous dissociation process, \( \beta = 2P_2(\cos \theta_m) \), where \( \theta_m \) is the molecular frame angle between the molecular transition dipole moment and the photofragment recoil direction, and \( P_2(\cos \chi) \) is the second-order Legendre polynomial. In a photodissociation process, following excitation via the electric transition dipole moments, namely,
parallel or perpendicular, would be expected to give a $\beta$ value of +2 or −1, respectively. The anisotropy 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 fumaryl chloride dissociation. Generally, an impulsive dissociation is accompanied with an anisotropic distribution of the photoproducts, since the dissociation lifetime is much shorter than the rotation period of the molecule. However, the anisotropy in an impulsive dissociation can be reduced, or wiped out, due to several factors, such as mixed initial transition with both parallel and perpendicular components, longer dissociation lifetime, dissociation not from a single geometry rather from a range of geometries etc. In fumaryl chloride, for C$_{2h}$ geometry, the $\pi$−$\pi^*$ transition, which has B$_2$, symmetry, the transition dipole moment is mainly along the x axis and $\gamma$ axis. The same is true for the n−$\pi^*$ transition. So, in this case even if there is a crossover from the initially prepared $\pi$−$\pi^*$ state to the n−$\pi^*$ state, the transition dipole moment is not changed. However, during this crossover period the molecule may rotate. The absence of recoil anisotropy in the present studies is expected mainly due to the mixed transition, as discussed, and the relatively longer dissociation lifetime, since the dissociation is not from the initially prepared state rather from the crossover state. In addition, the different geometries of fumaryl chloride also contribute to the $\beta$ value of ~0.0.

V. CONCLUSION

In summary, fumaryl chloride generates a chlorine atom upon excitation at 235 nm, which prepares the molecule initially in its $\pi$−$\pi^*$ state. The nascent distribution of the photofragment chlorine atom is measured by the 2 + 1 REMPI with the TOF mass spectrometry technique. We have determined the photofragment speed distribution, the anisotropy parameter $\beta$, and the spin−orbit branching ratio for the chlorine atom elimination channels, to gain insight into the dynamics of the chlorine atom formation. Polarization-dependent and state-specific TOF profiles are deconvoluted to get translational energy distributions, using a forward convolution method with least-squares fitting, taking into account the fragment anisotropies. The TOF profiles for Cl and Cl$^\dagger$ are independent of the laser polarization; i.e., the parameter $\beta$ is well characterized by a value of 0.0, within the experimental uncertainties. Two contributions, namely, the fast and the slow components, are observed in the translational energy distribution, $P(E_T)$, of Cl and Cl$^\dagger$ atoms formation channels. The average translational energies for the Cl and Cl$^\dagger$ channels for the fast component are 14.9 ± 1.6 and 16.8 ± 1.6 kcal/mol, respectively. Similarly, for the slow component, the average translational energies for the Cl and Cl$^\dagger$ channels are 3.4 ± 0.8 and 3.1 ± 0.8 kcal/mol, respectively. The energy partitioning into the translational mode is interpreted with the help of an impulsive model for the fast component, and a statistical model for the slow component. While the experimental $f_E$ value for a slow chlorine atom is nicely described with the statistical model, that for the fast Cl atom channel is slightly higher than the predicted value of 0.32, by the impulsive model. Apart from the chlorine atom elimination channel, the molecular HCl elimination is also observed in the photodissociation of fumaryl chloride. The observation of the HCl molecular elimination channel in the dissociation process and the bimodal translational energy distribution of the chlorine atom clearly indicate the existence of a crossover mechanism from the initially prepared state to the ground state. Finally, it is proposed that in fumaryl chloride the initially prepared S$_2$(1$\pi$−1$\pi^*$) state crosses over to various states, namely, S$_1$(1$n$−1$\pi^*$), (n−$\sigma^*$), and the ground state, and the Cl atom can be formed from all these states, with different values of $E_T$.

■ AUTHOR INFORMATION

*Electronic mail: haripu@barc.gov.in.

■ ACKNOWLEDGMENT

We thank Drs. S.K. Sarkar and T. Mukherjee for their constant guidance and keen interest throughout this work. We also acknowledge help rendered by Mr. Yogesh Indulkar during the initial experiments.

■ REFERENCES