Photoion-pair dissociation dynamics of polyatomic molecules with synchrotron radiation

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Positive–negative photoion pairs can be formed in the photoexcitation of molecules in the broad energy range from vacuum ultraviolet to soft X-ray. Synchrotron radiation is the most suitable photon source and state-of-the-art mass spectrometry techniques have been successfully applied in the experimental studies of such ion-pair photodissociation dynamics. This perspective will briefly review the recent progress on this topic and provide a general description of the mechanisms of ion-pair photodissociation dynamics of polyatomic molecules. Challenges in the understanding of ion-pair photodissociation in the higher photon energy range are also discussed.

1 Introduction

The photolysis of molecules, as a typical photochemistry reaction, has been widely investigated with various experimental techniques and theoretical methods, providing fundamental knowledge about molecular properties and basic thermochemical data. Positive and negative photoion pair dissociation is a novel photodissociation process, for example, for a diatomic molecule AB, $AB + h\nu \rightarrow A^+ + B^-$, and was first observed for the thallium halides when absorbing a vacuum ultraviolet (VUV) photon.\(^1\) The studies of this unimolecular dissociation have now been extended from simple diatomic molecules to polyatomic molecules, and in a broad energy range covering VUV, extreme ultraviolet (XUV), and soft X-ray. To gain an understanding of ion-pair dissociation dynamics, the basic thermochemical data of the target molecule and the fragment products, e.g., ionization potential (IP), electron affinity (EA), and dissociation energy ($D_0$), and the molecular potential energy surface (PES) at the excited or super-excited state are required. Conversely, precise measurements using specifically designed experimental techniques can provide not only these basic data, but also the dynamic details of the ion-pair dissociation.

Since the 1990s, many efforts have been made in experimental studies. The ion-pair photodissociation is endothermic and the energy of the absorbed photon is mostly in the VUV range. Therefore, tunable synchrotron radiation is the most suitable photon source for ion-pair photodissociation studies, although the successful application of VUV laser systems was recently reviewed by Suits and Hepburn.\(^2\) Their experimental work was based on two modern experimental techniques, ion velocity mapping (IVM) and threshold ion-pair production spectroscopy (TIPPS).\(^2\) Owing to the high resolutions of the IVM and the threshold pulse-field-induced dissociation techniques, the angular quantum number $J$-resolved spectra have been archived for several molecules.\(^2\) However, the limited tunability of the current VUV laser systems is still impeding their application in the broader and higher energy regions. During the past decades, experimental investigations of ion-pair photodissociation using tunable VUV synchrotron radiation have been conducted. In 1996, experimental approaches based on synchrotron radiation, especially the contributions of the groups of Mitsuke\(^3\)–\(^8\) and Baumgärtel,\(^9,10\) were reviewed by Berkowitz.\(^11\) Besides diatomic molecules, about twenty five polyatomic molecules were investigated and their thresholds of ion-pair dissociation were reported.\(^11\) More recently, Tuckett’s...
group at the University of Birmingham carried out a series of ion-pair photodissociation studies at the Daresbury SRS facility. Some new results for polyatomic molecules such as SF$_2$X (X = F, Cl, CF$_3$), small hydrocarbons, and the halogen derivatives of hydrocarbons have been summarized in their comprehensive review paper.$^{12}$ The reasons for writing this perspective paper are as follows. First, the previous reviews about the application of VUV synchrotron radiation on this topic$^{11,12}$ provided many experimental data for diatomic and polyatomic molecules, but the physical nature of ion-pair photodissociation was not generalized. Here more insights into the ion-pair photodissociation dynamics will be provided and a comprehensive review of its general features on the basis of recent experimental progress by different groups will be presented. Second, in combination with the VUV synchrotron radiation sources, a variety of experimental methods for this topic have been developed.$^{7,8,12-17}$ The merits and shortcomings of these experimental apparatuses should be evaluated, which may stimulate the development of more powerful techniques in the future and will be helpful for spectroscopists working on other topics. Third, although synchrotron radiation is a tunable photon source in the broad energy range, recent ion-pair photodissociation studies using the XUV and soft X-ray radiations$^{14,18-22}$ were ignored or received less attention in the previous reviews.$^{2,11,12}$ Here, the complicated dynamic mechanisms of the ion-pair photodissociation in this higher energy range will be discussed.

Detection of the anionic fragments of polyatomic molecules was initiated in the 1960s by using a discharge lamp coupled with a mass filter.$^{23}$ The ion-pair photodissociation of a triatomic molecule ABC can be described as,

$$ABC + hv \rightarrow AB^+ + C^-,$$  

$$\rightarrow A^+ + B + C^-,$$  

$$\rightarrow A + B^+ + C^-,$$  

$$\cdots$$  

In these different channels, the appearance energies (AE) of the anion C$^-$, AE(C$^-$), are determined by,

$$AE(C^-) \geq D_0(AB - C) + IP_a(AB) - EA(C),$$  

$$AE(C^-) \geq D_0(A - B - C) + IP_a(A) - EA(C),$$  

$$AE(C^-) \geq D_0(A - B - C) + IP_a(B) - EA(C),$$

where IP$_a$ is the adiabatic IP, the target ABC is assumed to be in its electronic and vibrational ground state, and the zero-point vibrational dissociation energy $D_0$ is used. The thermal correction to the dissociation energy should be considered in eqn (2) if the target molecule in the experiments is not cool enough. More details about thermochemical aspects of the photoion-pair formation energy can be found in a recent review.$^{12}$ Here we pay more attention to the formation of the ion-pair states and the related dissociation dynamics for polyatomic molecules.

The ion-pair state is a pseudo-bound state, also named as the “heavy Rydberg state”$^{24}$ describing an electrostatic interaction between the positive and negative fragments in the Rydberg-like structured molecule.$^{25}$ This shallow electrostatic attractive well, e.g., about ten wavenumbers of the well depth for an H$^+\text{H}^-$ ion-pair state,$^{24}$ is embedded on the nearly flat PES, and easily breached by the electric field of ion lenses used in the mass spectrometer. Two formation mechanisms, direct and indirect, of ion-pair states were proposed.$^{12}$ However, the pseudo-bound photoion-pair state cannot be detected directly because its shallow PES well is always far away from the equilibrium structure of molecule. In other words, the overlap between the ground state and this pseudo-bound state is very small for the vertical transition in the Franck–Condon region. As shown in Fig. 1, for case 1, the target is usually pumped to the repulsive wall of a potential energy profile in the Franck–Condon region, leading to a fast direct ion-pair dissociation, ABC $+ hv \rightarrow A^+ + B + C^-.$

In contrast, quite a few photoion-pair states can be prepared indirectly. For cases 2 and 3 in Fig. 1, if there is a coupling between the photoion-pair state and the stable parent cationic state, a photoion-pair dissociation might occur. In principle, the photoion-pair states in the TIPPS experiments$^2$ should be prepared as described by cases 2 and 3. Specifically, in case 2, when the molecule is pumped to one or several Rydberg states (e.g., $n = 10, 9, 8, \ldots; l = 0 (s), 1 (p), 2 (d), \ldots$, where $n$ and $l$ are the principal quantum number and the angular quantum number, respectively) that converge to a certain rovibrational state of a cationic (ABC)$^+, E = IP_a - \frac{\hbar}{(n-\delta)^2}$. Here IP$^+$ is the vertical IP of this rovibrational state of (ABC)$^+$, $R$ is the Rydberg constant, and $\delta$ is the quantum defect. The A$^+$, B, and C$^-$ fragments can be produced via the coupling between these Rydberg states and the ion-pair state. In case 3, if the molecule is pumped to one or several vibrational states (e.g., in the B–C bond stretching mode) of (ABC)$^+$, the fragmentation
products AB\(^+\) and C\(^-\) can be formed via couplings between these vibrational states and the ion-pair state. In contrast to the diatomic molecule, different vibrational modes of the polyatomic molecule may be involved in case 3. Obviously, the cross sections of the photoion-pair state and the dissociation yields are highly dependent on the curve crossings in the Franck–Condon region for cases 2 and 3. In fact, these photoion-pair states are competing with the other predominant decaying pathways, since the PESs at the different eigenstates would be likely to avoid the nonadiabatic crossings; moreover, the autoionization and radiative decay of these states would occur much faster. Alternatively, these excited states may decay to the neutral fragmentations, or the ionization dissociations. For a polyatomic molecule, the cross section ratio, \(\sigma_{\text{ion-pair}}/\sigma_{\text{photoionization}}\) is about \(10^{-2} - 10^{-5}\), which is usually much smaller than that for a diatomic molecule.\(^1\)

Besides the much smaller cross section of the photoion-pair dissociation, the spectral profile of the anion yield in the photoion-pair dissociation is distinctly different from that of the cation yield in the photoionization dissociation. A straightforward way to quantity the efficiency of the photoionization dissociation is to record the cationic product signal as a function of the photon energy. Usually the intensity of the cationic product is enhanced progressively with the energy increase in some range, which is depicted as the photoion efficiency (PIE) curve in Fig. 2(a). This gradually increasing profile shows the integral measurements of the cation signals, and the AE value of a cationic fragment can be determined with the onset of the spectral profile. To tell the ion-pair dissociation from the photoionization dissociation, the production of an anion rather than a cation is recorded in terms of the photon energy, namely, the ion-pair anion efficiency spectrum (IPAES) is recorded. As shown in Fig. 2(b–d), there are a variety of IPAES profiles that are distinctly different from the PIE curve. A diffuse band observed in the IPAES usually indicates the direct or fast ion-pair dissociation (case 1), in which the spectral onset corresponds to the AE(C\(^-\)) of channel (1c); A series of peaks with contracting energy intervals exhibit the Rydberg-state coupling mechanism (case 2), and these Rydberg series converge to a certain IP\(_v\). If some excited vibrational states strongly couple with the ion-pair state, a set of uniformly spaced peaks will stand out in the IPAES (case 3). As discussed above, the anion signals for cases 2 and 3 appear as the resonant-peak structures in the IPAES. Surprisingly, these spectral structures can be abruptly observed in some photon energy ranges, while there are almost no signals at the lower and higher energies. This means that a specific ion-pair dissociation window happens to occur in this energy range, which is a remarkable feature of the IPAES in comparison with the PIE curve.

2 Experimental technique developments

Challenges to detect the anionic fragments produced in ion-pair photodissociation are: (1) the very small cross sections demand the high sensitivity of the mass spectrometer used in experiments; (2) using the thermochemical data and eqn (2), the AE or threshold value for some ion-pair dissociations can be estimated prior to the experiments. However, the appearance of an anion in an IPAES is still frequently unpredictable because the ion-pair dissociation may be kinetically unfavorable (i.e., some energy barrier must be overcome) but thermodynamically permitted.\(^12\) In practice, it is necessary to search for anionic signals in a broad photon energy range, thus synchrotron radiation is the best candidate photon source. (3) The following process, named as dissociative electron attachment (DEA), frequently interferes with photoion-pair dissociation at the energy above the ionization threshold (i.e., IP\(_a\)),

\[
e^- + ABC \rightarrow (ABC)^- \rightarrow AB + C^-,
\]

where \(e^-\) is the low-energy photoelectron produced in the photoionization \(ABC + hv \rightarrow (ABC)^+ + e^-\). This secondary process can be effectively depressed by reducing the concentration of ABC in the reaction area.\(^12,16,17\) At the synchrotron radiation facilities of different countries, various anion-detection techniques have been developed for ion-pair photodissociation studies.

2.1 Quadrupole and time-of-flight anion mass spectrometers

A straightforward strategy is to utilize a quadrupole mass filter for the anion detection. To date, the application of a quadrupole mass filter is still very popular owing to its easy accessibility and compact construction. In Fig. 3, two typical experimental arrangements for ion-pair dissociation studies are shown and they were used in combination with the photon sources at the UVSOR facility in Japan (Fig. 3a)\(^9\) and at the Daresbury Laboratory in the UK (Fig. 3b).\(^12\) In these two apparatuses, the effusive molecular beam (MB) is perpendicular to the VUV light beam, and the anionic yields are extracted directly, then pass through the exit slit of the reaction area and the ion lenses. A channel electron multiplier is used to detect the anions. A small aperture or slit is usually placed at the joint between the reaction area (e.g., gas cell) or reaction chamber and detection chamber for the differential pumping. However, this arrangement may substantially reduce the quantity of the anions reaching the detector. Normally the ion...
detection efficiency of a quadrupole mass filter is estimated to be no more than 40% of the total production.

When the photon energy is above the IPa of the target molecule during the extraction of the anions from the reaction area, the photoelectrons can enter the quadrupole mass filter but be shaken out by the radio-frequency electrical field. The spurious signals of anions in the IPAES experiment are the result of the contamination of the DEA process. As shown in Fig. 4(a), the ion signals of N$_3^-$(m/z 42 a.u.) and CH$_3^+$(m/z 15 a.u.) show that the ion-pair dissociation, CH$_3$N$_3^+ + hv \rightarrow CH_3^+ + N_3^-$, can occur at an energy lower than the threshold of the dissociative ionization, CH$_3$N$_3^+ + hv \rightarrow CH_3^+ + N_3^- + e^-$ (12.87 eV), but higher than the ionization threshold (IE(CH$_3$N$_3^+$) noted in the Fig. 4).

If only ion-pair dissociation occurs in this energy range, the subtracted curve for CH$_3$N$_3^- - CH_3^+ = N_3^-$(the solid line in Fig. 4b) should be the same as that of the anion N$_3^-$ (the green line in Fig. 4a). The distinct difference between these two curves should be attributable to the DEA to CH$_3$N$_3^+$, CH$_3$N$_3^+ + e^-$ (photoelectron) → CH$_3^+ + N_3^-$. A simple and reasonable method has been successfully used by Tuckett’s group and ours. Namely, the ion-pair dissociation overwhelming the DEA process can be confirmed by the observation of the linear increase in the signal of C$^-$ with the concentration or pressure of ABC. Meanwhile, we made more improvements by using time-of-flight (TOF) anion mass spectrometry. As shown in the upper panel of Fig. 5, our home-made reflectron TOF mass spectrometer at the Hefei synchrotron radiation facility has been successfully used in ion-pair photodissociation studies.

Although the time structure of Hefei synchrotron radiation is a pseudo-continuum, the careful design of both the pulsed voltages and the time sequence applied to the ion lenses of the reflectron TOF lets us effectively record the high mass-resolution spectra of both the cationic and anionic fragments.

In our experimental apparatus, the VUV photon beam from an undulator is monochromatized by a spherical grating monochromator (made by Horiba Jobin Yvon in France) then focused onto the photodissociation region. An effusive molecular beam (MB) is introduced by a stainless steel tube with a diameter of 0.5 mm. The anionic fragments are collected with the reflectron TOF mass spectrometer (see the upper panel of Fig. 5 and ref. 17), which is perpendicular to the plane containing the molecular beam and the photon beam. The total length of the ion flight tube is 1400 mm. Packets of anions are pushed periodically from the ionization region by a pulsed repeller (lens 1) with voltage $-165$ V (1.5–2.0 μs pulse width and 18000 Hz repetition) into an acceleration region, wherein they are accelerated by an electrostatic field of 1000 V. But even in the absence of the repeller pulse and when no potential gradient exists in the extraction region, some ions enter the acceleration region owing to the existence of leakage fields. This reduces the signal-to-noise ratio. The more serious background noise arising from an abundance of photoelectrons can be effectively restrained by the low DC negative voltages, typically of $-0.04$ V and $-0.45$ V, added onto lenses 1 and 2. The photoelectrons can be moved out quickly, but the heavy anionic fragments remain in the space between lenses 1 and 2.
The pulsed anion beam is focused (900 V) and transferred through the drift area (floated on 1000 V), then reflected by the retarding lenses (the last lens is on \(-460\) V). Finally, the anions are detected with two zigzag stacking microchannel plates. It is noted that the collection efficiency of the anionic fragments reaches nearly 90% owing to the large aperture of the lenses (with diameters of 20 mm) and the high pulsed voltage of \(-165\) V on lens 1. Here, the kinetic energies of the anionic fragments gained from the photodissociation are supposed to be less than 2 eV. This is based on the fact that the physical nature of ion-pair photodissociation is a resonant-like process, i.e., when the photon energy is far from the threshold of a given dissociation channel, this channel may be closed. As shown in the lower panel of Fig. 5, the high ion-collection efficiency of our reflectron TOF mass spectrometer enables us to observe many anionic fragments produced in the ion-pair dissociation of CHCl₃.

2.2 Coincidence and imaging spectroscopy studies

As represented in eqn (1), different cationic fragments can be produced in the ion-pair photodissociation of a polyatomic molecule. The IPAES of C⁺ provides overall information of the channels (1a), (1b), (1c), etc., but the different dissociation channels cannot be identified. The positive ion-negative ion coincidence (PINICO) technique has been developed by Mitsuke et al. at the UVSOR facility. In the PINICO experiments, the positive ion (AB⁺, A⁺, or B⁺) and negative ion (anion C⁻) were accelerated to opposite sides and analyzed by the respective TOF mass spectrometers. The arrival time of the anionic or cationic fragment is used as the start time in the coincidence experiment, then according to the flight-time...
difference between these two oppositely charged ions, a specific ion-pair dissociation channel can be investigated.

The kinetic energy and angular distribution of negative ions are of the utmost importance not only in the determination of the electronic characteristics of the relevant excited states, but also in the exploration of ion-pair photodissociation dynamics. Using a linear two-field TOF mass spectrometer (Wiley–McLaren design), one can obtain the translational energy of a fragment ion by measuring its flight time from the reaction region to the detector. The angular distribution of the ion can be measured by the rotating mass spectrometer in a conventional turn-table arrangement, but some angular directions are difficult to access due to the geometrical limitations. The complete three-dimensional momentum distributions of the anionic fragment can be obtained using the recently developed IVM technique. The first application of the IVM technique in this field was reported for alkyl halides using the third harmonic of a Nd:YAG laser. Recently, F images from CH$_3$F were recorded at a free electron laser facility, in which the photoelectrons can be filtered out by a gated data accumulation coinciding with the slow laser pulse repetitions. However, this method encounters some difficulties due to the very high frequency of the synchrotron radiation. As shown in Fig. 6(a), at the UVSOR facility Hikosaka and Shigemasa developed an IVM spectrometer to detect the anionic fragments of the ion-pair dissociation. They used a permanent magnetic field installed around the reaction area to suppress the influence of the photoelectrons. Fig. 6(b) shows the total O$^-$ yield curve (solid line) and the O$^-$ images from O$_2$, in which two peeled images of O$^-$ recorded around the threshold of the ion-pair dissociation to O$^-$($^1$P) + O$^-$($^3$P) exhibited significant differences in their momentum distributions. A more sophisticated imaging method, the positive-negative ion coincidence IVM technique, has also been developed for the ion-pair photodissociation studies. However, the image quality of those coincidence experiments is not high, perhaps due to the low flux of the monochromatized light from a discharge lamp. It is noted that a magnetic field was also utilized to eliminate the interferences of accidental coincidences between the scattered cation and the photoelectron.

3. Recent progress in the study of ion-pair dissociation dynamics of polyatomic molecules

Anion mass spectrometry is the most efficient and straightforward technique applied in this topic. Therefore, here more attention is paid to the mass spectra of anionic fragments. Two subsections presented in the following will focus on ion-pair dissociation in two different photon energy ranges, namely, VUV and soft X-rays. As the minor process competing with photoionization and double ionization, the ion-pair dissociation carries plenty of dynamics information about excited and super-excited states of polyatomic molecules.

3.1 Excitations with vacuum ultraviolet photons

Recently, ion-pair photodissociation of CHCl$_3$ has been investigated using the reflectron TOF mass spectrometer in our group and the quadrupole mass filter by Tuckett et al. As shown in Fig. 7(a), we recorded the IPAES of Cl$^-$ in a broad energy range, and some fine structures were present here that were not observed by Tuckett et al., perhaps due to the higher ion-collection efficiency of our reflectron TOF mass spectrometer. As discussed above for case 3 (see Fig. 7(b)), the fine spectral structures of band F3 in the energy range of 12.20–12.80 eV have been tentatively assigned with two sets of vibrational progressions $\nu_2$ (CCl$_3$ symmetrical stretching mode) and $\nu_2 + \nu_3$ ($\nu_3$ is the CCl$_3$ symmetrical deformation) of the cationic core of the high Rydberg-state molecule. In a similar scenario, another two sets of vibrational progressions $\nu_4$ (C–H bending mode) and $\nu_4 + \nu_2$ can be assigned for band F5 in Fig. 7(c). This work demonstrated that during the photoexcitations, the couplings between molecular vibrations and electron transitions are very strong and such a nonadiabatic process dramatically enhances the cross sections of the ion-pair dissociations. For this molecule, a novel ion-pair...
photodissociation process has also been found. As shown in Fig. 7(a), the additional band F4 at 14.55 eV may be attributed to a cascade process: the Cl2 species at the ion-pair excited state D0 2 3Pg can be directly produced by the photolysis of CCl3H, then this metastable state decays through the ion-pair dissociation Cl2 (D0 2 3Pg )- Cl + + Cl0, which can be induced by the strong pulsed field (field strength B 16 500 V m−1) employed in our reflectron TOF mass spectrometer. This peak was also observed in the spectrum (at 14.7 eV) that was recorded with the quadrupole anion mass filter,12 but was very weak, perhaps due to the low efficiency of the pulse-field-induced dissociation in that apparatus (in which a very low electrostatic field was applied through the reaction region, see Fig. 3b and ref. 12).

The high ion-detection efficiency of the reflectron TOF mass spectrometer gives an insight into the dissociation dynamics in case 3.17 The ion-pair photodissociation described as case 2 also become observable, even for large polyatomic molecules. For the two largest molecules, the Rydberg series of Cl− for benzyl chloride (C6H5CH2Cl, shown in Fig. 8b)16 are much more pronounced in the spectrum than those of H+ for neo-pentane (neo-C5H12, shown in Fig. 8a).6 In the latter, a quadrupole mass filter was used. The mechanisms of cases 2 and 3 may be observed together in an IPAES. In our recent work for 2/3-monochlorothiophenes, see Fig. 9, both the vibrational structures and the Rydberg series have been observed.32 However, these vibrational structures were not well-resolved due to limited energy-resolution and too many vibrational modes being involved in the dissociations.

In the IPAES experiment, there are always several photoion-pair states to be populated. If only very few (or even one) photoion-pair states can be prepared, for example, as in the TIPPS experiment,2 the spectral structure of the anion product will become well-resolved. However, the TIPPS technique combined with synchrotron radiation is still unavailable in our group, primarily due to the low flux of the second-generation Hefei synchrotron radiation. The application of this experimental method in our group will be hopefully achieved after updating the present Hefei synchrotron radiation facility.

In our reflectron TOF mass spectrometer, the collection efficiencies are assumed to be united for the different anions because of the low kinetic energy of most of the anionic fragments (less than 2 eV), the large apertures of the lenses, and the high negative-voltage pulse applied on lens 1 (see Fig. 5).
Therefore, for CF2Cl2, the production efficiencies of F/C0 and Cl/C0 should be comparable. As shown in Fig. 10, these two products were found to be comparable in the photon energy range of 17.25–20.50 eV. They happened to have an equivalent production efficiency around the ionization threshold of H2 B1 (19.15 eV). It is difficult for us to identify the different contributions to these curves because a lot of many-body dissociations may be involved. The PINICO technique may be suitable for identifying the preferred dissociation channels.

3.2 Near double-ionization thresholds and inner-shell electron excitations

When the photon energy is extended to higher regions, the ion-pair dissociation becomes much more complicated. For example, in the photoexcitations of the inner valence orbitals of SO2, a new onset of O− signals showed a common threshold with the doubly-charged fragment cation SO2+, implying a process, \( h\nu + SO_2 \rightarrow (SO_2^+) \rightarrow SO^{2+} + O^- + e^- \). However, as shown in Fig. 11(a), the ion-pair dissociation processes to O− and H− (or D−) of molecular water are more complicated. At photon energies lower than the double ionization threshold (double IP), two sets of 2\(\Sigma_1\) states were assigned with multi-electron shake-up processes including excitation to virtual or Rydberg orbitals. Above 32 eV, both O− and H− (or D−) were proposed to be produced via the singly or doubly positively charged parent cation. It is interesting that an exceptional significant isotope effect on the cross section ratio of H\(\Sigma_1\):D\(\Sigma_1\) was observed in Fig. 11(b). The authors explained that the asymmetric bond stretching O–H (or O–D) in the dication H2 O2+ (or D2 O2+) led to the dissociations. Electron correlation usually plays a role in the electron excitations around the double IP. In this energy range, if the ion-pair dissociation is coupled with the doubly excited state, the cation product is usually multiply charged (e.g., AB\(2^+\), AB\(3^+\)) and undergoes further dissociation.

For highly symmetrical molecules, the electron-excitation induced ion-pair dissociation is quite an interesting topic. For sulfur fluoride (SF6, in Oh symmetry), the spatial overlap between the valence and virtual molecular orbitals (MO) is strong in the inner well (see Fig. 12a). If the electron is promoted to the virtual MOs such as 6\(\sigma_1\), 5\(\pi_1\), 4\(\pi_6\), or 2\(\pi_5\), shape resonance will be formed, while the couplings between these valence MOs and Rydberg orbitals such as 4s, 5s, etc. are

![Fig. 9](image_url) The IPAES of Cl− produced in the photoexcitation of 2-monochlorothiophene. This figure is adapted from ref. 32 with the copyright permission of ACS.

![Fig. 10](image_url) Competition between Cl− and F− productions in the photoexcitation of CF2Cl2 with high-energy photons. This figure is adapted from ref. 33 with the copyright permission of Elsevier, B.V.

![Fig. 11](image_url) (a) The anion yield spectra of O− from H2O and D2O and (b) the anion yield spectra for H− and D− from H2O and D2O. Two sets of 2\(\Sigma_1\) states denote the multi-electron transitions and the short vertical lines represent the double ionization potentials. These figures are adapted from ref. 14 with the copyright permission of IOP.
relatively weak (similar to case 2 discussed earlier). Therefore, as shown in Fig. 12(b), the bands of F\(^{-}\)/C\(_{0}\), F\(_{2}\)/C\(_{0}\), and SF\(^{-}\)/C\(_{0}\) assigned with shape resonances are broader and stronger than those assigned with Rydbergs. In the energy range of 30–40 eV, the strongest peaks of F\(^{-}\) and F\(_{2}\)/C\(_{0}\) in the IPAES are attributed to the valence transitions 3\(t_{1u}\) \(\rightarrow\) 6\(t_{1g}\) and 2\(e_{g}\) and 4\(a_{1g}\) \(\rightarrow\) 6\(t_{1u}\) and their shake-up states.\(^{19}\) Except for their distinctly different spectral profiles, the correlations of the peak positions can be established between the threshold photoelectron spectrum (TPES) and the IPAES of F\(^{-}\)/C\(_{0}\), implying that the common intermediate states were monitored.\(^{19}\) In contrast to the IPAES of F\(^{-}\) and F\(_{2}\)/C\(_{0}\), the spectrum of SF\(^{-}\)/C\(_{0}\) displayed two strong peaks centered at 38 and 45 eV. The polar ion-pair complex of SF\(^{-}\)/C\(_{0}\)–F\(^{+}\) as the precursor was proposed for the SF\(^{-}\)/C\(_{0}\) yields.\(^{19}\)

Different decay mechanisms are associated with the ion-pair dissociation for the inner-shell excited molecule. As shown in Fig. 13, besides the shake-up states of the electron transitions Cl\(_{2}\)\(p\) \(\rightarrow\) 13\(a_{1}\) (antibond C–Cl*) and 14\(a_{1}\) (antibond C–F*), the Rydberg series converging to the spin–orbit split 2\(p\)\(_{3/2}\) and 2\(p\)\(_{1/2}\) were assigned in the Cl\(^{-}\) yield curve for CF\(_{2}\)Cl\(_{2}\).\(^{20}\) It is noted that in contrast to the single electron excitation in case 2, multi-electron excitations are involved in the present Rydberg series. If spectator Auger decay is responsible for the anion fragmentation, the inner-shell excited CF\(_{2}\)Cl\(_{2}\)* may undergo the following process,\(^{20}\)

\[
\text{CF}_2\text{Cl}_2 + h\nu \rightarrow (\text{CF}_2\text{Cl}_2)^* \rightarrow (\text{CF}_2\text{Cl}_2)^* + e_{\text{Auger}} \rightarrow \text{CF}_2\text{Cl}_2^{2+} + \text{Cl}^- + e_{\text{Auger}}^{-}.\]

Above the Cl\(_{2}\)\(p\) ionization threshold, the process may be,\(^{20}\)

\[
\text{CF}_2\text{Cl}_2 + h\nu \rightarrow (\text{CF}_2\text{Cl}_2)^* + e_{\text{photoelectron}} \rightarrow (\text{CF}_2\text{Cl}_2)^{3+} + \text{Cl}^- + e_{\text{photoelectron}}^{-} + e_{\text{Auger}}^{-},\]

in which (CF\(_{2}\)Cl\(_{2}\)*)\(^{+}\) represents the cation CF\(_{2}\)Cl\(_{2}\)\(^{+}\) at a super-excited state. The Cl\(^{-}\) may also be produced via ultra-fast direct dissociation prior to Auger decay.\(^{20}\)

Near the ionization threshold of inner-shell electrons, the Coulombic interaction between the slow threshold photoelectron and a more energetic Auger electron, the so-called post-collision interaction (PCI), causes an energy loss of the Auger electron.\(^{21}\) Meanwhile, the threshold photoelectron is further retarded and recaptured by the molecular cation into a Rydberg orbital, which is called a PCI-mediated shake-down process. This new Rydberg electron may be captured by the departing Cl atom during dissociation, leading to the enhancement of the Cl\(^{-}\) yields. This interesting process is depicted in Fig. 14 and is believed to play an essential role in the ion-pair dissociation of inner-shell excited ClCl\(_{2}\), CHCl\(_{3}\), and CH\(_{2}\)Cl\(_{2}\).\(^{22,34}\) The ion-pair dissociation studies of inner-shell excited polyatomic molecules have been extended to Freons,\(^{20,35}\) CH\(_{2}\)Cl\(_{2}\), SiF\(_{4}\), SiCl\(_{4}\), Si\(_{2}\)H\(_{2}\)X (X = O, S),\(^{39}\) and so on.

Similar to the ion-pair dissociations around the double IP, the enhancement of anionic fragmentation in inner-shell excited molecules may be also associated with the doubly excited states near the inner-shell ionization threshold. As shown in Fig. 13, the shake-up states related to the transitions Cl\(_{2}\)\(p\) \(\rightarrow\) 13\(a_{1}\) and 14\(a_{1}\) can be categorized into this mechanism, although they

**Fig. 12** (a) Effective molecular potential acting on an excited electron of SF\(_{6}\), and (b) anionic yields in the inner valence region and the threshold photoelectron spectrum (TPES). In the TPES, a, b, and c represent the transitions 3\(t_{1u}\) \(\rightarrow\) 6\(t_{1g}\), 2\(e_{g}\) \(\rightarrow\) 6\(t_{1u}\), and 4\(a_{1g}\) \(\rightarrow\) 6\(t_{1u}\) respectively. These figures are adapted from ref. 19 with the copyright permission of IOP.
have minor contributions to the Cl$^-$ yields. No resonant structures for F$^-$ were observed in the inner-shell excitation Cl 2p of CF$_2$Cl$_2$ and CFC$_3$, implying that the core-electron hole is localized at the Cl atoms and cannot transfer to another ligand F atom. In contrast, in the S 2p excitation of SF$_6$, the spectral profiles of F$^-$ and S$^-$ come to resemble each other. This localized hole mechanism is also invalid in the vicinity of the Cl 2p inner-shell ionization of CF$_2$Cl because of the observations of similar anion yield curves of C$^-$, F$^-$, and Cl$^-$. Under the low bunch mode operation of the Spring-8 synchrotron radiation, the momentum distributions of O$^-$ have been recorded with the IVM method in the vicinity of the C 1s and O 1s ionization thresholds of CO$_2$. The inner-shell region formation of negative ions is 4 or 5 orders of magnitude lower than that of the photoelectron, therefore, a magnetic field was still used to eliminate the accidental coincidences between the scattered cation and the photoelectron. Below the C 1s and O 1s ionization thresholds, Hikosaka et al. recorded the O$^-$ velocity images for the 1s → π* transitions and Rydberg series; while above the thresholds, the different anisotropic distributions indicated that the ion-pair dissociations should be attributed to two doubly excited states.

4 Conclusions and outlook

Ion-pair dissociation is a very special decay path of the molecule at excited states. Many studies reported recently have proved that its dynamic mechanism is much more complicated for polyatomic molecules than for diatomic molecules. In the VUV photon energy range, the molecular Rydberg and vibrational excited states within the single-electron transition scheme are frequently seen to couple with the ion-pair states, corresponding to the resonant peaks or bands in the anion production efficiency spectra. The electron correlation effect becomes more significant at higher photon energies, thus it is still a challenge to obtain details of the ion-pair dissociation dynamics for the inner-shell excited molecules. State-of-the-art mass spectrometry techniques combined with a synchrotron radiation source have been powerful tools in experimental studies, although a complete understanding of the anion mass spectra still requires the aid of other spectroscopies such as photoabsorption and photoelectron spectroscopy. Further development of experimental methods based on the synchrotron radiation facility is required. Two experimental routes are under our consideration: the PINICO method (possibly in combination with an IVM technique) can provide us with more insight into the multi-channel ion-pair photodissociation of polyatomic molecules; J state-resolved photoion-pair dissociation experiments for some simple molecules may be achieved by using the TIPPS method at the updated Hefei synchrotron radiation facility in the future.

Although the cross section of the ion-pair dissociations is much smaller than that of the other decay paths at the molecular excited states, the former can occur in a very broad energy range from the region below the first ionization threshold to the region around inner-shell electron ionizations. Positively and negatively charged fragments (possibly together with neutral radicals), as the yields of the ion-pair dissociation of polyatomic molecules, are usually active in chemistry and potentially trigger the subsequent chemical reactions with the surrounding matter. The energetics and dynamics of ion-pair photodissociation are indispensable for a complete understanding of photochemistry and related fields.
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