Accounts

Formation and Dissociation Dynamics of Molecular Superexcited States

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This is a survey of recent progress in experimental studies of spectroscopy and dynamics of molecules in the superexcited states. The Platzman's concept of the superexcited states deduced from the theoretical analysis of the interaction of ionizing radiation with matter has been recently substantiated experimentally. Most of the observed superexcited states are assigned to high Rydberg states which are vibrationally (and/or rotationally), doubly, or inner-core excited, and converge to each ion state. Non-Rydberg superexcited states are also observed. The dissociation dynamics of these states as well as the products are very different from those of the lower states excited below ionization thresholds. The neutral dissociation is unexpectedly more important than ionization. Molecular superexcited states are described as reaction intermediates in some fundamentally important collision processes, e.g., electron-ion or ion-ion recombination, Penning ionization, and electron attachment, and are described also as important species in the primary processes of radiation chemistry, VUV-photochemistry, and plasmas. Comments are presented on molecular superexcited states in the condensed phase. Finally, the future perspectives of the present studies are summarized.

The Platzman's concept[1,2] of the superexcited states deduced from the theoretical analysis of the interaction of ionizing radiation with matter has been recently substantiated experimentally due to long-term spectroscopy and dynamics studies since the early 1970s of the dissociative excitation of molecules in photonic and electronic collisions with molecules.[3–12] These studies are classified as follows in terms of the ways to produce superexcited states:

(1) Electron impact spectroscopy,
(2) Discharge-lamp photon impact spectroscopy,
(3) Laser photon impact spectroscopy,
(4) Synchrotron radiation photon impact spectroscopy, and
(5) Coincident electron-energy-loss spectroscopy.

Electron beams and discharge-lamp photons were mainly used in the 1960s and 1970s, and also still now, for this purpose.[3,9,12] An earlier part of such studies was motivated by the present author's chemical studies pointing out an important role of superexcited states for the first time experimentally in the primary processes of hydrocarbon radiation chemistry.[13–16] After the 1980s, laser multiphotons and synchrotron radiation (SR) have also been used. Details of the electronic states of superexcited molecules, at least in the optically allowed states and the mechanism of their autoionization and dissociation have been quickly clarified mainly by means of SR as an excitation source.[3–11] The coincident electron-energy-loss spectroscopy has been further developed recently as a new experimental method for molecular superexcited states in the optically forbidden states.[10,17–21] Among all these studies our group has pioneered those of (1), (4), and (5).

The spectroscopy and dynamics of the formation and decay processes of molecular superexcited states, particularly the neutral dissociation process, have been recently surveyed comprehensively by the present author and his co-workers.[3–11] These reviews and feature articles conclude that superexcited states are molecular high Rydberg states, converging to each ion state, which are vibrationally/rotationally, doubly, or inner-core excited. Non-Rydberg superexcited states are also observed. The dissociation dynamics as well as the products of dissociation of these states are very different from those of the lower states excited below about ionization thresholds. Another important conclusion is that molecules are, in general, not easily ionized. Neutral dissociation is unexpectedly more important than ionization when molecules absorb energy in the region above their ionization thresholds. The present article introduces some currently important features of these conclusions with some examples of molecules, the related remarks, and the future perspectives.

1. Interaction of Photons with Molecules

The absorption of a single photon by a molecule in the electronically ground state changes its electronic state from the ground state to a final excited or ionized state. Its transition probability is expressed in terms of the optical oscillator strength f_j as:[3]

$$f_j(E_j) = (E_j/R)M_j^2, \tag{1}$$

where E_j is the excitation energy to form the state j and R, the Rydberg energy, and M_j^2, the dipole matrix element in atomic units squared for the state j formation. The total sum of the oscillator strengths including discrete and continuous spectra is equal to the total number Z of electrons in the molecule, viz.:

$$\sum_j f_j(E_j) + \int_I^\infty (\mathrm{d}f/\mathrm{d}E)\mathrm{d}E = Z. \tag{2}$$

This is the Thomas–Kuhn–Reiche (TKR) sum rule, where I represents the first ionization potential or the ionization threshold of a molecule, and $\mathrm{d}f/\mathrm{d}E$ is the oscillator strength distribution which is proportional to the photoabsorption cross section σ_t at the energy E.

A decisive step in the physical and physicochemical stages of the action of any ionizing radiation, i.e., high-energy photons, electrons, ions or neutrals, on matter is collisions of secondary electrons in a wide energy range with molecules.[22–25] Ionization and excitation of molecules in collisions with electrons in the energy range higher than 10^2 eV are well elucidated by the Born–Bethe theory.[26] It is also shown that a radiation chemical yield, G_j, the number of product species in the state j formed per 100 eV energy absorbed, is approximately proportional to $M_j{}^2$ as follows:[1,3,16,22–25]

$$G_j = (100/W)(M_j{}^2/M_i{}^2), \tag{3}$$

where W is the mean energy, measured in eV, for the production of an ion pair and $M_i{}^2$ is the dipole matrix element squared for ionization, i.e.,

$$M_i{}^2 = \int_I^\infty \eta(E)\frac{R}{E}\frac{\mathrm{d}f}{\mathrm{d}E}\mathrm{d}E, \tag{4}$$

where $\eta(E)$ is the quantum yield for ionization at the excitation energy E. Since

$$\eta(E) = \sigma_i(E)/\sigma_t(E), \tag{5}$$

where $\sigma_i(E)$ is the photoionization cross section. Equation 3 called the optical approximation, means that the radiation chemical yield G_j is obtained from optical cross section data. The optical approximation as well as the approximation in the Born-Bethe theory are reasonable when they are not applied to a narrow specific excitation-energy range near its threshold where optically forbidden transitions are relatively important in comparison with optically allowed ones but rather applied to a wide excitation-energy range. Optical cross section data are, therefore, of fundamental importance in understanding not only the interaction of photons with molecules, but also the action of any ionizing radiation with matter.[22–25]

Oscillator-strength values had long been measured for various molecules in wavelength regions at least longer than the near ultraviolet (UV) region, whereas until recently measurements in the wavelength region shorter than the cutoff of LiF as a window at 105 nm, at which the photon energy is 11.8 eV, were relatively few because of experimental difficulties in obtaining appropriate photon sources and because no suitable window materials were available. The cutoff energy of 11.8 eV, roughly speaking, corresponds to or exists near the ionization potentials of commonly occurring molecules. The sum of the oscillator strengths below 11.8 eV amounts to only a few percent of the total sum, which is equal to Z according to Eq. 2. The absorptions in the vacuum ultraviolet and soft X-ray (VUV-SX) region are much stronger than those in all other wavelength regions. Since there have been remarkable advances in SR research and the related experimental techniques in the VUV-SX region, a great many of measurements in this region are now available.[3–11] Such a situation of SR as a photon source is summarized in Fig. 1.[3,5,22,23,25]

Figure 1 shows the wavelengths of electromagnetic radiation from the infrared to the γ-ray regions and corresponding photon energies. Characteristic X-rays, ^{60}Co-γ rays, and VUV

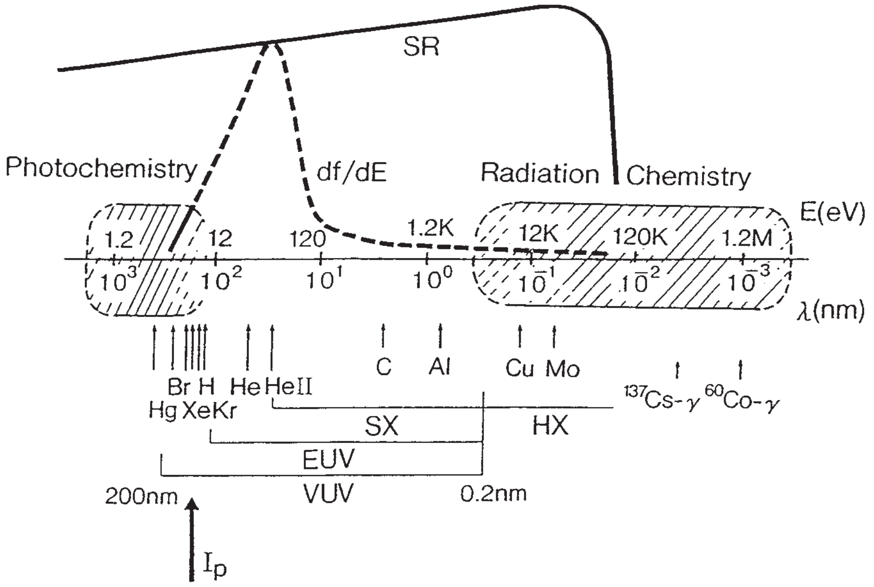

Fig. 1. Synchrotron radiation (SR) chemistry as a bridge between radiation chemistry and photochemistry. The oscillator strength distribution $\mathrm{d}f/\mathrm{d}E$ is shown as a function of wavelength λ and photon energy E. Note the relation $E\cdot\lambda = 1.24 \times 10^3$ (eV·nm). The intensity of SR is also shown, as are the energies of photons from several line sources. VUV, EUV, SX, and HX stand for vacuum ultraviolet, extreme ultraviolet, soft X-ray, and hard X-ray, respectively.[3,5,22,23,25]

light from discharge lamps are indicated by the arrows. Figure 1 shows that the wavelength range or the definition of VUV is quite different from those used previously for a relatively much longer wavelength range in VUV-photochemistry and includes also SX. The shaded areas indicate regions for which photon sources, apart from SR, are available and these areas correspond to photochemistry and radiation chemistry. Figure 1 clearly demonstrates that SR bridges the wide gap in the photon energy between photochemistry and radiation chemistry, i.e., ''photon-collision chemistry'' and ''electron-collision chemistry,'' respectively.

The absorption of energy by a molecule in the electronically ground state changes its electronic state from the ground state to a final excited or ionized state as follows:[3,4]

$$\mathrm{AB} \rightarrow \mathrm{AB}^+ + \mathrm{e}^- \quad \text{direct ionization} \tag{6}$$

$$\rightarrow \mathrm{AB}' \quad \text{superexcitation} \tag{7}$$

$$\rightarrow \mathrm{AB}^* \quad \text{excitation} \tag{8}$$

$$\mathrm{AB}' \rightarrow \mathrm{AB}^+ + \mathrm{e}^- \quad \text{autoionization} \tag{9}$$

$$\rightarrow \mathrm{A} + \mathrm{B} \quad \text{dissociation} \tag{10}$$

$$\rightarrow \mathrm{AB}'' \quad \text{processes other than (9) and (10).} \tag{11}$$

When a molecule AB receives energy which is larger than its I, AB is directly ionized and is excited to form AB′, which was named by Platzman a ''superexcited'' molecule.[1,2] The superexcited AB′ can ionize or dissociate into neutral fragments. Since η is defined by Eq. 5 in case of the energy supplied by photoabsorption, the value of $1 - \eta$ shows the importance of the dissociation process in the total decay channels of AB′ because the processes 11 may not be so important in the decay of such extremely highly excited states. One of the processes 11, ion-pair formation: $\mathrm{AB}' \rightarrow \mathrm{A}^+ + \mathrm{B}^-$, has been extensively studied to clarify the dynamics of superexcited molecules, although its cross section is much smaller than those of the processes 9 and 10.[3] The value of η is, therefore, smaller than unity in the energy range even above I, which means that the molecules excited into this energy range are not always ionized but can use their energy for processes other than ionization. Therefore, σ_t is the sum of the cross sections for the processes 6, 7, and 8, and σ_i is the sum of the cross sections for the processes 6 and 9. The cross section for the process 10 is thus given by $\sigma_t - \sigma_i (= \sigma_d)$.[3]

2. Dissociation of Superexcited States of Simple Molecules

Primary and secondary processes following photoabsorption of molecules in the VUV-SX region are strongly influenced by superexcited states. Among various decay processes of molecular superexcited states, the dissociation process 10, i.e., the neutral dissociation, in competition with autoionization has been shown to play an important role in the VUV-SX photochemistry. This could be called the synchrotron radiation chemistry, as clearly shown in Fig. 1. The difficulties of detecting neutral products, however, hampered the experimental investigation of neutral dissociation. Thus, in the region far beyond the ionization threshold, most of the experimental studies had been restricted to those of photoionization, i.e., the measurements of photo-electrons and -ions, and the measurements of photoabsorption spectra. Since, however, such studies are not so sensitive to superexcitation owing to a huge contribution from direct ionization, most of the superexcited states, especially those having repulsive potential curves or surfaces, had not yet been revealed even in diatomic molecules.

A careful and comprehensive survey has been conducted of the potential-energy curves or surfaces of simple molecules such as H_2, D_2, N_2, O_2, and CO and of the related spectroscopy and dynamics data on the interactions of photons and electrons with these molecules. This survey shows that there has been, in fact, very little information even for such simple molecules on the superexcited states, i.e., on the neutral excited states in the excitation-energy range above the ionization thresholds, in particular on their dissociation dynamics.[3,4,27]

The observation of the neutral dissociation of simple molecules by detecting undispersed fluorescence from excited fragments using optical filters has been shown to be a useful tool for studying the decay of superexcited states.[3,8,9,28] This fluorescence technique has made it possible to get the information on repulsive potential structures of superexcited states as well as on well-defined vibrational, in some cases further rotational, levels of bound superexcited states.[3,8,9] However, it has not provided detailed information on particular dissociation products and precise dissociation limits, which is indispensable for understanding the dissociation and autoionization dynamics of molecular superexcited states.

A powerful new experimental method, the two-dimensional fluorescence spectroscopy, has therefore been developed to reveal a bird-eye view of the neutral dissociation dynamics of molecular superexcited states over a wide excitation energy range.[29] In the two-dimensional fluorescence spectroscopy, the yield spectra of dispersed fluorescence radiation or the dispersed fluorescence excitation spectra emitted from neutral fragments produced by the dissociation of molecular superexcited states have been simultaneously measured as a function of the excitation wavelength of SR over a wide range. This method has been applied to simple diatomic and triatomic molecules.[29–33] The potential-energy curves or surfaces as well as their dissociation dynamics, which are vibrationally, in some cases further rotationally, energy-resolved, have been thus substantiated experimentally for the first time.

In the two-dimensional spectroscopy of the dissociation dynamics of state resolved molecular superexcited states, monochromatized SR is focused into a gas cell that contains target molecules. VUV fluorescence emitted from dissociation fragments produced from superexcited states is dispersed, as shown in Fig. 2, by a secondary monochromator equipped with a holographic grating. A fluorescence spectrum is recorded using a resistive anode-type position sensitive detector (PSD) behind a microchannel plate (MCP).[29,30]

Since the spectroscopy and dynamics of the superexcited states of molecular hydrogen/deuterium and other simple molecules have been comprehensively surveyed in detail elsewhere,[3–12] these are only briefly introduced below with some examples.

Figure 2 shows an example of the two-dimensional fluorescence excitation spectra emitted from dissociatively excited neutral oxygen atoms, O*, which are formed in the photoexci-

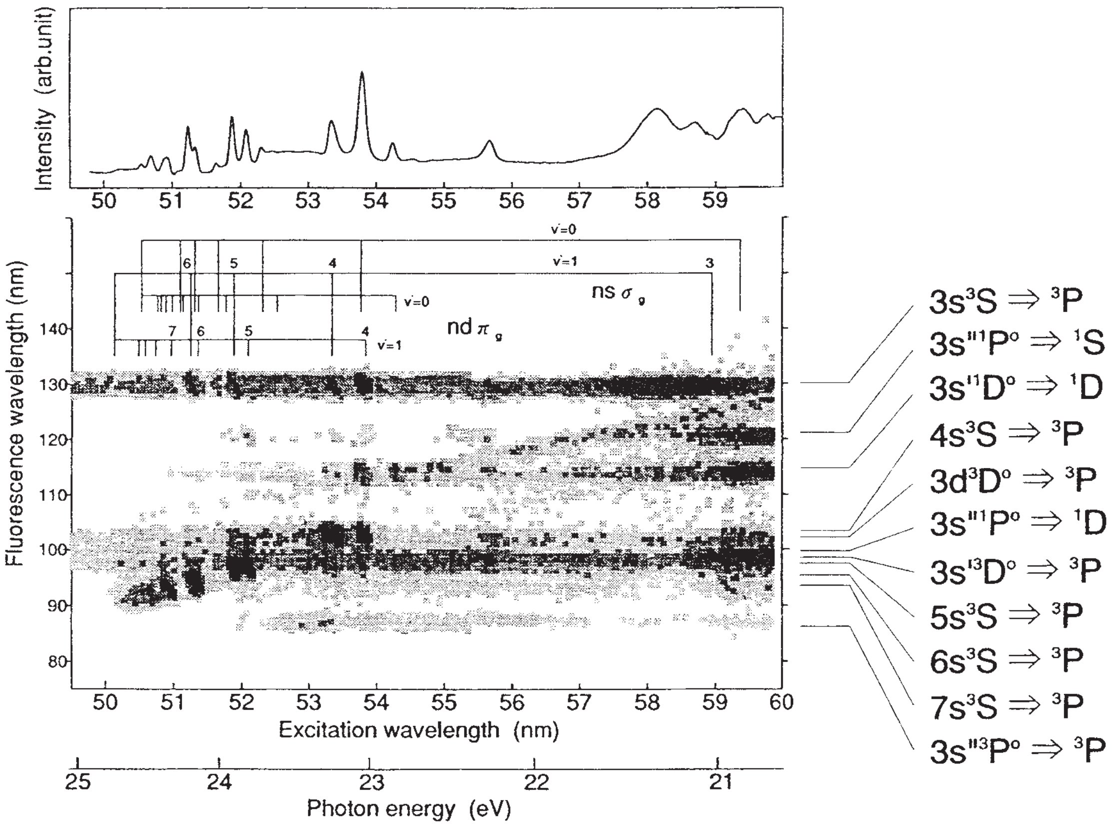

Fig. 2. Two-dimensional fluorescence spectrum of excited O^* atoms produced from the neutral dissociation of superexcited O_2^{**} as a function of both the excitation wavelength for $50 \leq \lambda_{ex} \leq 60$ nm and fluorescence wavelength for $80 \leq \lambda_f \leq 140$ nm (lower panel) in the photoexcitation of O_2.[29] The fluorescence yields presented by the grey rectangle plots increase from white to black linearly with 8 steps of the color. Horizontal line structures present the partial fluorescence yields of OI radiation lines. A non-dispersed fluorescence spectrum for $105 \leq \lambda_f \leq 180$ nm (upper panel) is shown together.

tation of O_2 as a function of the excitation wavelength λ_{ex} for $50 \leq \lambda_{ex} \leq 60$ nm (the photon energy 24.8–20 eV).[29] Each of the horizontal line structures in Fig. 2 presents the partial fluorescence yield from individual O^* atoms produced in the neutral dissociation of superexcited molecular oxygen O_2^{**}. Figure 2 shows clearly the following two types of striking behavior of the dissociation dynamics of vibrationally resolved superexcited molecular oxygen. One is the state-to-state selective neutral dissociation, in which the n quantum number is conserved,

$$O_2^{**}(c^4\Sigma_u^- ns\sigma_g \text{ or } nd\pi_g) \rightarrow O^*(ns^3S) + O(^3P). \qquad (12)$$

The other is a vibrationally selective neutral dissociation. In the process 12, the dissociation of the $v' = 1$ state of O_2^{**} is much more enhanced than that of the $v' = 0$ state of O_2^{**}. This is clear evidence for a vibrationally resolved tunneling predissociation.

The two-dimensional spectroscopy has been applied also to the dissociation dynamics of superexcited states of CO.[31–33] New results have been obtained also of the preferential dissociation of the vibrationally excited Rydberg states. It is interesting that all the observed fluorescences are assigned to those emitted from fragment carbon atoms although those emitted from fragment oxygen atoms are energetically possible.

Thus the two-dimensional spectroscopy is a powerful method to study the dissociation dynamics at least of diatomic molecules in the superexcited states. The two-dimensional spectroscopy has been further applied also to a triatomic molecule N_2O,[30] providing new information on the spectroscopy and dissociation dynamics of state-assigned superexcited states of N_2O. Figure 3 shows an example of the two-dimensional fluorescence spectroscopy of N_2O as a function of both the excitation photon energy in the range between 14.28 and 36.35 eV and the fluorescence wavelength in the range between 80 and 200 nm. Such spectra provide detailed information on the neutral dissociation of superexcited states of N_2O. Each rectangular dot represents the yield of dispersed fluorescence in exponentially increasing order from light to dark with 20 degrees of gradation. Ionization potentials for some of the one-electron ionic states are also indicated in Fig. 3. Diagonal structures in the spectrum are due to scattered primary light, which appear at higher order positions of the secondary monochromator. The final dissociation products, dissociation limits, and correlation among neutral dissociation potentials of N_2O have been identified. In most cases of the neutral dissociation of superexcited N_2O formed by photoexcitation below 20 eV, it has been shown that the superexcited states undergo multistep predissociation. The neutral dissociation of the $nd\pi$ Rydberg states converging to $N_2O^+(C^2\Sigma^+)$ has shown different behavior from other Rydberg states. The $nd\pi$ Rydberg states preferentially dissociate into $N^*(5d^sL) + NO(X^2\Pi)$. This has been explained by the dissociative character of the

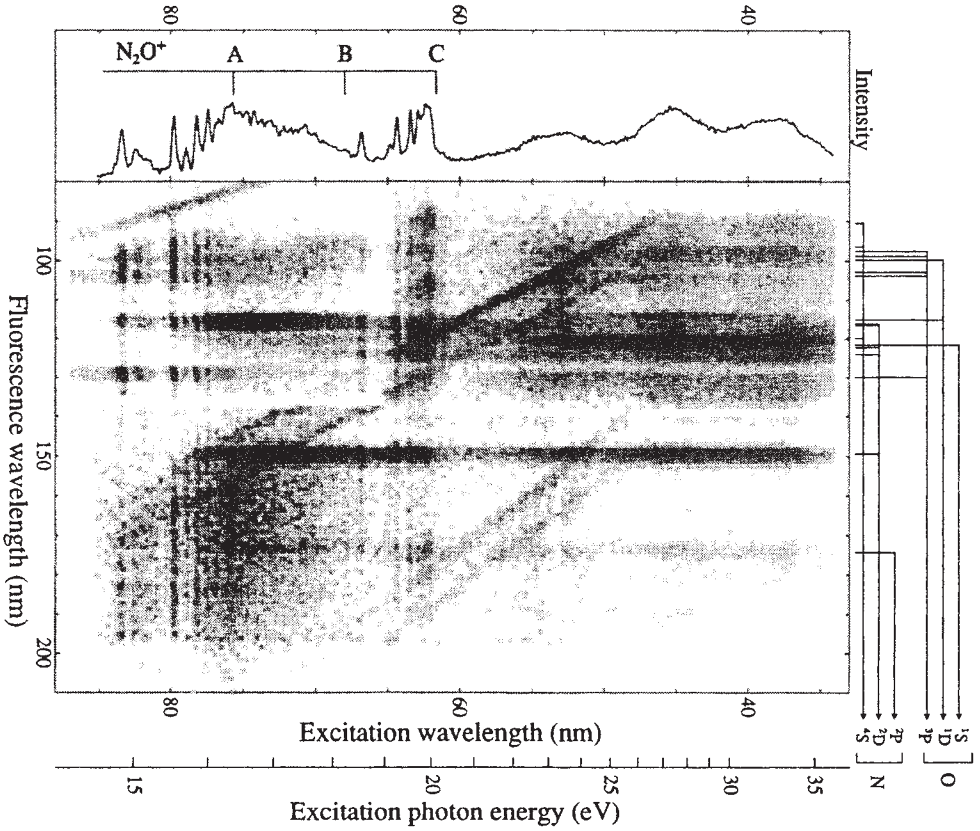

Fig. 3. Two-dimensional fluorescence excitation spectrum of excited O* and N* atoms produced from the neutral dissociation of superexcited N_2O^{**} in the photoexcitation of N_2O.[30] The spectrum is divided into two parts. One is a spectrum as a function of both the excitation photon energy in the range of 14.28–36.35 eV and the fluorescence in the range of 80–140 nm. The other is a spectrum as a function of both the excitation photon energy in the range of 14.57–36.35 eV and the fluorescence wavelength in the range of 140–200 nm. The fluorescence intensity in the spectrum increases exponentially from light to dark. The total fluorescence yield curve is also shown in the left portion of the figure, of which intensity is on a linear scale. The positions of the fluorescence lines are indicated at the top of the figure.

precursor Rydberg states based on the core ion model. The neutral dissociation into $N_2(a^1\Pi_g) + O$ has also been shown to switch to a three-body neutral dissociation. Broad features of the enhanced fluorescence observed in the excitation photon energy range above 20 eV have been identified as clearly due to multiply excited neutral states.

3. VUV-Optical Oscillator Strength Distributions and Photoionization Quantum Yields of Polyatomic Molecules

To understand the dynamics of superexcited states of molecules, in general, it is necessary to measure absolute cross sections of photoabsorption, photoionization, and neutral dissociation processes as well as absolute photoionization quantum yields.[3–11] These cross section values had been measured for a variety of molecules only in the wavelength region longer than the LiF cutoff at 105 nm, while cross section values in the wavelength region shorter than the LiF cutoff at 105 nm had been very few. After the developments of the dedicated SR facilities and related new experimental techniques, however, those cross section values for both simple and polyatomic molecules have been measured[3–10] and critically compiled.[11] When the TKR sum rule is compared with the sum of the obtained σ_t or f_j values for a molecule in the wavelength region longer than 105 nm which corresponds, roughly speaking, to about the first ionization potential of most molecules, it is found that the sum of the obtained f_j values corresponds to only less than a few percent of the value of Z. It is, therefore, concluded that the interaction of a photon with a molecule in the VUV-SX region, where SR is the most promising photon source as clearly shown in Fig. 1, is predominant over all the other wavelength regions.[3–11]

Optical oscillator strength distribution is, therefore, of fundamental importance in understanding the interaction of photons with molecules, providing the important information about energy spectra for the formation of superexcited states.[3–11] Instead of measuring these cross sections for a variety of complex molecules at random, these cross sections for molecules in several stereo-isomer series have been systematically measured and compared with one another or with the sum rule.[34–37] The main purpose of such a systematic investigation is to see how $\mathrm{d}f/\mathrm{d}E$ changes with changing molecular structures. Since isomer molecules consist of the same kind and the same number of atoms, the $\mathrm{d}f/\mathrm{d}E$ of isomers was expected to have the following properties:[34–37]

(1) The sum of $\mathrm{d}f/\mathrm{d}E$ of one isomer over all the energy region was expected to be equal to that of another isomer, and also to the number of electrons in the molecule, according to the TKR sum rule.

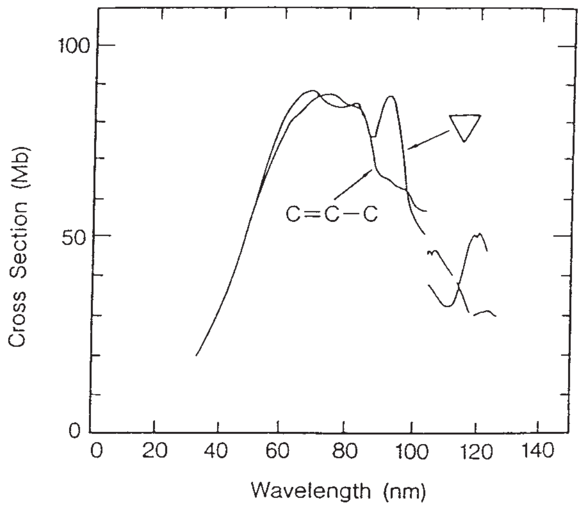

Fig. 4. Absorption cross sections of cyclopropane and propene.[34] Gaps in the cross section curves at about 100 nm are attributed to the following reasons. The curves in the longer wavelength region are obtained using a gas cell with LiF as a window, while those in the shorter wavelength region are obtained using a gas cell without window (see text).

(2) The gross features of the df/dE of isomers were expected to be almost identical with each other in the wavelength region where inner-core electrons were excited, because the molecular structure of isomers would have relatively little influence on the excitation of inner-core electrons. Moreover, the value of df/dE in such a wavelength region would be almost equal to the sum of the df/dE values of the constituent atoms.

With the above-mentioned expectations, the photoabsorption cross sections have been measured for sets of isomers:[34–37] C_3H_6 (cyclopropane and propene), C_4H_8 (1-butene, isobutene, *cis*-2-butene, and *trans*-2-butene), C_6H_{12} (cyclohexane, 1-hexene, and tetramethylethene), C_2H_6O (ethyl alcohol and dimethyl ether), and C_3H_8O (propyl alcohol, isopropyl alcohol, and ethyl methyl ether) in the wavelength region from about 30 to 140 nm. Results are compared with one another and with the sum rule from the above viewpoints. Figure 4 shows, as an example, the absorption cross sections, i.e., the oscillator strength distributions of the C_3H_6 isomer molecules, cyclopropane and propene.[34] Similar cross section data have also been obtained for the other isomer series listed above, allowing the common new features of absorption cross sections or oscillator-strength distributions to be summarized as follows:

(1) The σ_t values show a maximum at about 70–80 nm (about 16–18 eV) for each molecule.

(2) In the wavelength region shorter than that at the maximum the σ_t values are almost the same among the isomer molecules, e.g., cyclopropane and propene as shown in Fig. 4, and are equal to the sum of the cross sections for the constituent atoms.

(3) In the longer wavelength region, the cross sections have different peaks and shoulders depending on the isomer, i.e., on its molecular structure as shown again in Fig. 4. The sum of the cross sections in this wavelength region is, however, almost equal among the isomer molecules, which means, therefore, that the total oscillator-strength distribution normalized to Z according to the TKR sum rule can be divided to the two regions, i.e., the longer and shorter wavelength regions. It also means that the sum of the oscillator strengths in each region does not depend on the molecular structure of an isomer and is constant among the isomer molecules; in other words, that the partial sum rule satisfies the oscillator-strength distribution in each region.

Table 1. Sum of the Oscillator Strength Distributions of C_3H_6[34]

Wavelength/nm	Cyclopropane	Propene
Below Ip	0.746	0.507
Ip–105	0.715	0.666
105–35	11.744	12.176
35 >	10.251	
Total	23.46	23.60
Z	24	

The oscillator strength value in the shortest wavelength region is obtained by a semiempirical theory, while the other values in the longer wavelength regions are obtained experimentally (see text and Ref. 34). The accuracy of these values in their absolute magnitudes should be examined further in detail.

These results have made an important contribution to chemical physics and physical chemistry[3–11] particularly to motivate the development of new quantum chemistry,[38] and have also made a helpful contribution to radiation research in estimating the energy deposition spectra of molecules in the interaction of ionizing radiation with molecules.[22–25] The results, e.g., those in Fig. 4, well satisfy the TKR sum rule as summarized in Table 1.[34] The agreement is extremely good between the sum of the obtained oscillator strength values partly including semiempirical ones in the higher-energy region and the number of electrons, Z. Table 1 also clearly shows that the sum of the oscillator-strength distributions in the energy region below the first ionization potential occupies only a few percent of the total and that the distributions in the VUV-SX region are thus of great importance in understanding the ionization and excitation of molecules.

A photoionization quantum yield η, which is the absolute photoionization probability of an atom or a molecule on a single photoabsorption event or the magnitude of the number of electrons which are produced from a molecule absorbing a single photon, is the quantity of a considerable importance to evaluate photoabsorption processes above the first ionization potential, i.e., a competition between direct ionization and excitation to the superexcited states opening to autoionization and dissociation. The measurement of η is, therefore, of great importance for further characterizing superexcited states. It had been extremely difficult, however, to measure absolute η-values.

It has become possible recently to measure absolute photoionization quantum yields, as well as the absolute photoabsorption cross sections, of C_3H_6, C_4H_8, C_6H_{12}, C_2H_6O, and C_3H_8O isomers by a newly established method using SR as a light source and a multiple-staged photoionization chamber equipped with thin metal foil window.

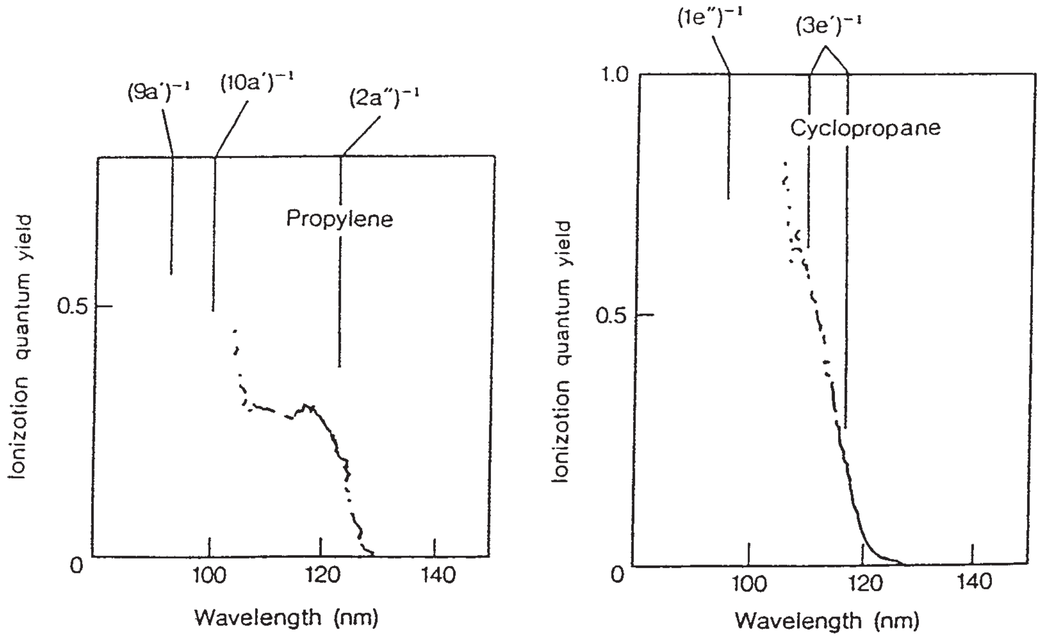

Fig. 5. Photoionization quantum yields of C_3H_6 isomers.[36]

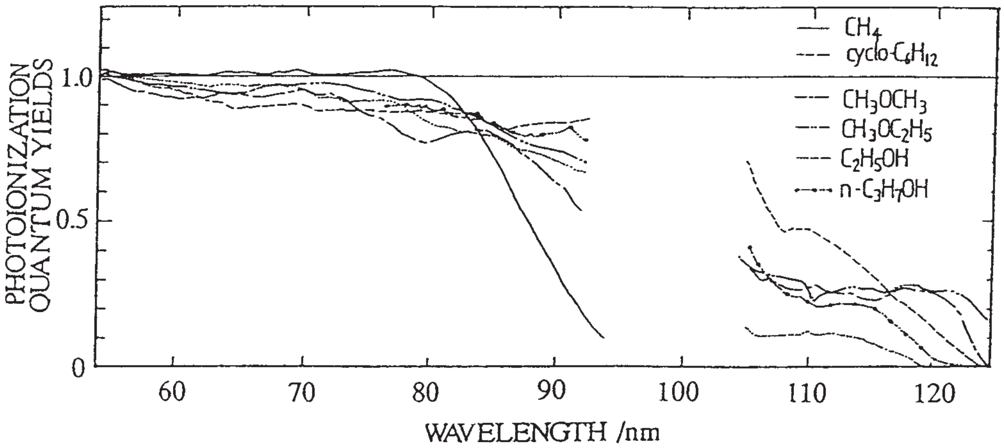

Fig. 6. Photoionization quantum yields of several molecules.[3] Gaps in the curves in the wavelength region between 92 nm and 105 nm are attributed to a lack of appropriate thin metal filters to remove a second order light.

Figure 5 shows, for example, the η-curves for cyclopropane and propene.[36] These are very different from each other; the curve for cyclopropane increases almost monotonically and much more steeply than that for propene, which increases and shows a step or a shoulder with decreasing wavelength. The obtained η-curves for these molecules show common new features as functions of wavelength or photon energy; the energy difference between the first and the second ionization potentials correlates well with the shape of the η-curves. The larger energy difference corresponds to the longer step length. This result means that the η-value increases steeply in the wavelength or energy region just close to the ionization potential, and is explained by the conclusion that the most important part of the superexcited states is high-Rydberg states converging to each ion state.

Figure 6 shows the ionization quantum yields for some polyatomic molecules measured in the wavelength region of 54–92 nm, together with those in the wavelength region longer than 105 nm.[3] No data are shown in the wavelength region between the two because there is practically no thin metal window which is convenient for the measurement of ionization quantum yields and because there exists a relatively large effect of higher order light in this wavelength region. The results may be summarized as follows:

(1) η-Values in the region above, but close to, the first ionization potential are much less than unity. This means that most molecules are not easily ionized even when they have a sufficient amount of their internal energies to be ionized. In this region, therefore, the neutral fragmentation of superexcited molecules is of great importance in the total decay channels.

(2) η-Values do not reach unity even in the energy range more than about 10 eV above the first ionization potential.

(3) η-Values increase with increasing photon energy and reach unity in the absolute scale at the energy range above about 23 eV (or 54 nm).

(4) η-Curves show interesting structures.

We conclude from these results that non-ionizing processes, such as the neutral fragmentation of superexcited molecules, have an important role in their decay channels. Since there exists an important part of the magnitude of the oscillator strength distributions of most molecules in the wavelength range of 60–100 nm in which the η-values are clearly and largely deviated from unity, we conclude in general that molecules are not easily ionized but are dissociated into neutral fragments even when they have energies much larger than their ionization thresholds.

4. Dissociation of Superexcited States of Polyatomic Molecules

Neutral fragments formed from the dissociation of superexcited molecules often have excess energies electronically, vibrationally, rotationally, and/or translationally excited, because the photon energies corresponding to the wavelengths in Fig. 6 are much higher than the bond dissociation energies to form fragments in their ground states. It is, therefore, of great interest to observe optical emissions from excited fragments as a function of wavelength, i.e., to obtain excitation spectra of optical emission and to compare with the structures in η-curves. In the following, hydrocarbons are chosen as an example from recent experiments of a variety of kinds of polyatomic molecules[3–11] for such a comparison to clarify in detail the spectroscopy and dynamics of superexcited polyatomic molecules.

The photoionization quantum yields of acetylene are compared in Fig. 7 with the excitation spectra of fluorescence from excited fragments produced in the dissociation of a superexcited acetylene molecule, providing a conclusion of the observed dissociation processes as follows:[39]

$$C_2H_2 + h\nu \rightarrow C_2(d^3\Pi_g) + 2H \tag{13}$$

$$C_2(C^1\Pi_g) + 2H \tag{14}$$

$$CH(A^2\Delta) + CH \text{ (or } CH(A^2\Delta)) \tag{15}$$

$$H(2p) + C_2H \text{ (or } C_2 + H) \tag{16}$$

The precursor superexcited states for these dissociation processes 13–16 have been assigned in detail to high Rydberg states and/or inner valence excited states which have been investigated theoretically.

The excitation spectrum in Fig. 7(d) as well as the corresponding dissociation 15 is of particular interest from chemical viewpoints because of a predominant breaking of the triple bond of acetylene in a specific energy range, which reminds the present author of a theoretical investigation[40] indicating a predominant breaking of the double bond of ethylene in interpreting the hydrogen isotope effect on η. A critical comment was presented on this conclusion based on experimental results of the radiolysis of C_2H_4 and C_2H_4-Ar systems.[41]

Similar studies of olefin and paraffin hydrocarbons are going on to substantiate the electronic states and dissociation dynamics of the superexcited states of these molecules.[42] Figure 8 shows, for example, the absolute σ_t, σ_i, and σ_d values of methane as a function of the photon energy. The σ_d curve clearly shows that there exist superexcited states in the energy range of 13–16 eV and in the range of 19–24 eV. Expanded views in these energy ranges are shown in Figs. 9 and 10, respectively. In Fig. 9 the vibrational progressions with spacing of about 0.10–0.15 eV are observed as superimposed on the broad continuum and are assigned to the Rydberg states converging to the $(1t_2)^{-1}$ ion state. In Fig. 10 the vibrational progressions are also observed and are assigned to the Rydberg states converging to the $(2a_1)^{-1}$ ion state. Excitation spectra of fluorescence emitted from dissociation fragments produced from these state-assigned superexcited states are observed using the two-dimensional spectroscopy.

5. Other Related Remarks

Important roles of superexcited states have been considered theoretically and experimentally as reaction intermediates in a variety of elementary reaction processes or collision processes such as electron-ion and ion-ion recombination, Penning ionization, and electron attachment processes. The information, as summarized in this article, on the spectroscopy and dynamics of the formation and decay processes of molecular superexcited states is helpful for understanding the essential features of the dynamics of these collision processes.[3]

An important role of molecular superexcited states and the product dissociation fragments as reactive species in the radiolysis of molecular compounds was first presented theoretically by Platzman as his concept of the superexcited states[1,2] and was experimentally pointed out for the first time by the present author and co-workers.[13–16] These investigations and similar ones[43–45] in radiation chemistry and VUV-photochemistry had motivated many electron- and photon impact experiments, as described in the introduction, most of which have been pioneered again by the present author's group.[3–12] Based on the current status of the understanding of superexcited states, as described in the preceding sections, an important role of superexcited states may be considered reasonably also in other types of reaction systems such as various phenomena in ionized gases; electric discharge plasmas, particularly reactive plasmas such as chemical vapor deposition and etching,[46] and collisions in the upper atmosphere and planetary space.

The investigation of superexcited states in the condensed phase is closely related with that of ionization itself in the condensed phase.[3] It is a still unresolved important problem, as described below, to understand the ionization potential of condensed matter or to discriminate ionized states from highly excited states in the condensed phase. It is of great importance also to investigate in detail, as a related problem, geminate electron-ion pairs and high-Rydberg states in the condensed phase. It should be noted that a key experiment to clarify these problems, on which there have been very few reports, is the absolute measurement of ionization quantum yields in the condensed phase using synchrotron radiation.[3]

It has been pointed out that photoabsorption, photoionization and photodissociation cross section data are greatly needed for molecules not only in the liquid or solid phase but also in high density gases or cluster systems to substantiate superexcited states of molecules in the condensed phase.[3] Such cross-section data have been very few in comparison with those in the gas phase.[47] In radiation chemistry and related fields, however, interesting measurements have been re-

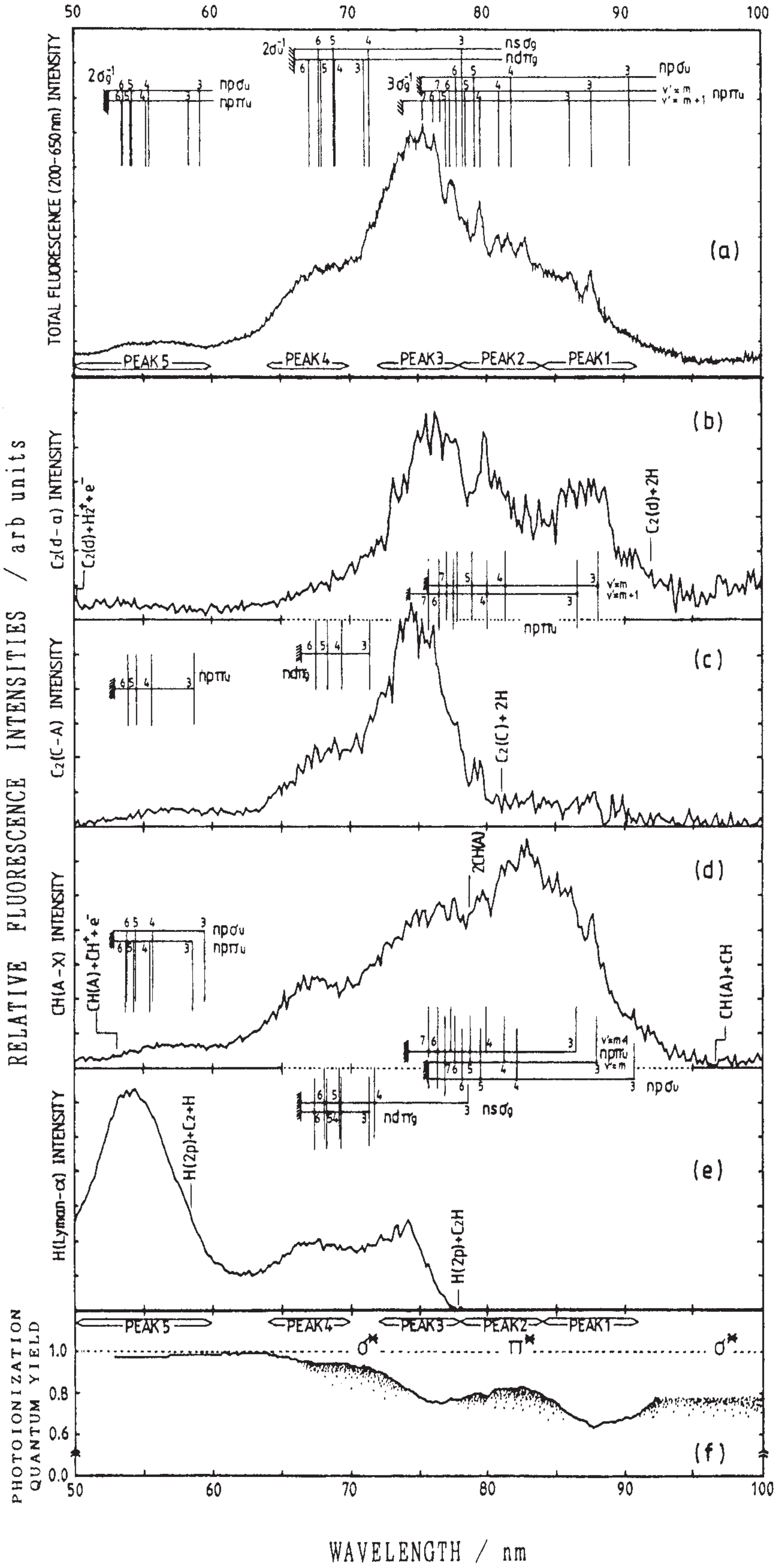

Fig. 7. Fluorescence excitation spectra for (a) the total emission in 200–650 nm detection range, (b) $C_2(d^3\Pi_g \rightarrow a^3\Pi_u, \Delta v = 0)$, (c) $C_2(C^1\Pi_g \rightarrow A^1\Pi_u, \Delta v = 1)$, (d) $CH(A^2\Delta \rightarrow X^2\Pi, 0 \rightarrow 0)$ and (e) Lyman-α from H(2p) (121.6 nm).[39]

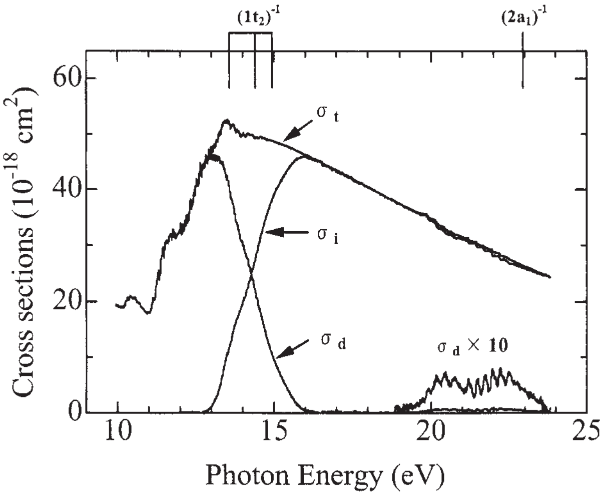

Fig. 8. Photoabsorption (σ_t), photoionization (σ_i), and photodissociation (σ_d) cross sections of CH_4 as a function of the photon energy.[42]

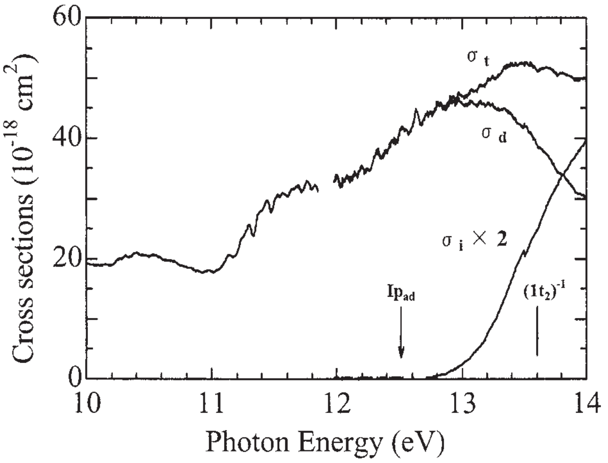

Fig. 9. An expanded view of Fig. 8 in the photon energy range of 10–14 eV to show clearly the vibrational progressions of the Rydberg states converging to the $(1t_2)^{-1}$ ion state.[42]

ported of the photoionization thresholds as well as of Rydberg states near the thresholds in liquids.[48–52] Photoionization studies of doped supercritical fluids are of also considerable importance to substantiate ionization mechanisms of molecules in the condensed phase.[53,54] Optical oscillator strength and related data have been measured extensively for a variety of organic and biological molecules in the condensed phase.[55–57] An important role of superexcited states has been considered also in the VUV-photolysis of biological systems.[58] It should be noted that a new method has been developed recently for the measurement of the oscillator strength distribution of liquids by inelastic X-ray (SR) scattering spectroscopy.[59–61] It is interesting to compare the oscillator strength distribution of gas phase water[62] with those of liquid water[59,60] and of amorphous ice.[63]

6. Conclusions and Future Perspectives

This article has summarized recent progress in experimental studies of the interaction of VUV-photons with molecules, i.e., those of photoabsorption, photoionization, and photodissociation of molecules in the excitation photon energy range of 10–50 eV with a particular emphasis placed on current understanding of the formation and dissociation dynamics studies of molecular superexcited states. Most of the observed molecular superexcited states are assigned to high Rydberg states which are vibrationally (and/or rotationally), doubly, or inner-core excited and converge to each ion state. Non-Rydberg states are also observed. Dissociation into neutral fragments in comparison with ionization is of unexpectedly great importance in the observed decay of each of these state-assigned superexcited molecules. Dissociation dynamics as well as its products of superexcited states are very different from those of lower excited states below about ionization thresholds. The obtained information as summarized above in this section is helpful for understanding the essential features of an important role of molecular superexcited states as reaction intermediates in some fundamental collision processes. Molecular superexcited states have an important role not only in the primary processes of radiolysis and VUV-photolysis but also in those of, more in general, various phenomena in ionized gases. Furthermore, molecular superexcited states in dense media such as high-density gases, clusters, liquids, and solids are discussed.

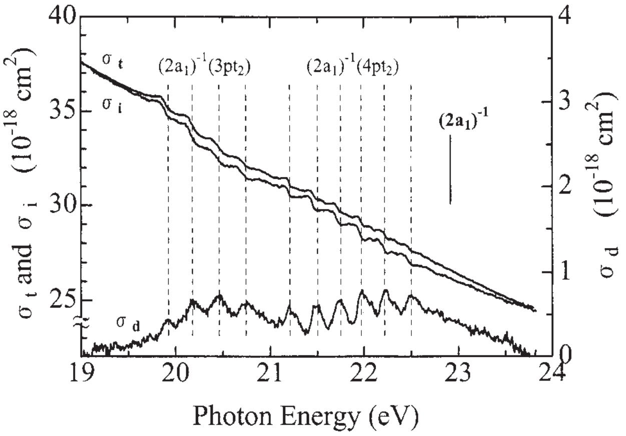

Fig. 10. An expanded view of Fig. 8 in the photon energy range of 19–24 eV to show clearly the vibrational progressions of the Rydberg states converging to the $(2a_1)^{-1}$ ion state.[42]

Some future problems needing more work from the viewpoints of the present article are as follows:

(1) Optically non-emissive fragments which may be formed more abundantly than emissive ones from the neutral dissociation of molecular superexcited states should be measured by combining lasers with SR.

(2) Since rotational-state resolved spectroscopy and dynamics studies of molecular superexcited states have been restricted to only a few molecules or specific excitation-energy ranges,[3,9] these studies should be extended to more in general a variety of molecules and wider excitation-energy ranges utilizing new SR facilities of next generation types, from which the newer essential features of the spectroscopy and dynamics of molecular superexcited states, for example, those of their dissociation lifetimes, may be obtained.[64]

(3) The coincident electron-energy-loss spectroscopy[10,17–21]

should be applied more to other molecules than H_2, D_2, and N_2 to study more in general the spectroscopy and dynamics of molecular superexcited states in the optically forbidden states.

(4) New theoretical approaches should be developed to elucidate the experimental results summarized in this article concerning the formation and dissociation dynamics of molecular superexcited states, for example, those of the dissociation dynamics of state-assigned molecular superexcited states particularly of doubly excited states while taking into account the breakdown of the Born–Oppenheimer approximation,[9,10] and those of absolute oscillator strength distributions.[3,38]

(5) The experimental methods summarized in this article should be applied more to larger molecules and also further to polymers.

(6) Synchrotron radiation should be applied more to molecules in dense media such as those in dense gases, clusters, liquids, and solids, and further to those at interfaces and surfaces to reveal the effects of intermolecular forces or molecular circumstances on the formation and decay dynamics of molecular superexcited states.[65] These experiments would contribute greatly to the substantiation of specific features of ionization and excitation phenomena in such dense media as opposed to those in low density gases.

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