VI-G  Photoionization and Photodissociation Dynamics
Studied by Electron and Fluorescence Spectroscopy

Molecular photoionization is a major phenomenon in vacuum UV excitation and provides a large amount of information on fundamental electron-core interactions in molecules. Especially, neutral resonance states become of main interest, since they often dominate photoabsorption cross sections and lead to various vibronic states which are inaccessible in direct ionization. We have developed a versatile machine for two-dimensional photoelectron spectroscopy in order to elucidate dynamical aspects of superexcited states such as autoionization, resonance Auger decay, predissociation, vibronic couplings, and internal conversion. In a two-dimensional photoelectron spectrum (2D-PES), the photoelectron yield is measured as a function of both photon energy $E_h\nu$ and electron kinetic energy $E_k$ (binding energy). The spectrum, usually represented as a contour plot, contains rich information on photoionization dynamics.

Photofragmentation into ionic and/or neutral species is also one of the most important phenomena in the vacuum UV excitation. In some cases, the fragments possess sufficient internal energy to de-excite radiatively by emitting UV or visible fluorescence. It is widely accepted that fluorescence spectroscopy is an important tool to determine the fragments and to clarify the mechanisms governing the dissociation processes of diatomic and polyatomic molecules. For several years we have concentrated our energies on fluorescence spectroscopy of H₂O in the photon energy region of 15–55 eV.

VI-G-1  Photofragmentation Mechanisms of H₂O
Studied by Ultraviolet Dispersed Spectroscopy

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Fragmentation of H₂O has been studied by dispersed fluorescence spectroscopy at excitation photon energies above 20 eV.¹ In dispersed spectra several vibrational bands begin to emerge below 320 nm with an appearance energy of $h\nu \approx 30$ eV. We have assigned these peaks to OH($A^2\Sigma^+ \rightarrow X^2\Pi$) transition, judging from characteristic peaks due to the $R_1$ band heads for the $\Delta v = v' - v'' = 0$ sequence at 306.4, 312.6, and 318.8 nm. The counter fragment of OH($A^2\Sigma^+$) must be H*($n \geq 2$) in the Rydberg state ($n \geq 2$). The above appearance energy is much higher than the dissociation limits for the OH($A^2\Sigma^+$) + H*($n \geq 2$) channels, but in good agreement with the vertical transition energies² for the associated Rydberg states of H₂O. There exist salient hydrogen atomic lines at $h\nu \geq 24.5$ eV constituting the Balmer series with $n = 3–9$, as indicated in Figure 1. The dispersed spectra reveal that there is no appreciable fluorescence signal from OH($A^2\Sigma^+$) below 30 eV. Hence, the dissociation channel of OH($A^2\Sigma^+$) + H*($n = 2$) is not responsible for the Balmer emission at $h\nu = 24.5–30$ eV. The most plausible process leading to this Balmer emission is the three-body dissociation to H*(n ≥ 3) + H(n = 1) + O(3 P g), which has the thermochemical threshold at 21.7 eV with n = 3.

References

VI-H  Extreme UV Photoionization Studies of Fullerenes by
Using a Grazing-Incidence Monochromator and High-
Temperature Mass Spectrometer

On the beam line BL2B in UVSOR a grazing incidence monochromator has been constructed which supplies photons in the energy region from 20 to 200 eV [M. Ono, H. Yoshida, H. Hattori and K. Mitsuke, Nucl. Instrum. Methods Phys. Res., Sect. A 467-468, 577–580 (2001)]. This monochromator has bridged the energy gap between
The absolute photoabsorption cross section of C\textsubscript{60} has been determined by means of mass spectrometry with the photon source of monochromatized synchrotron radiation of $h\nu = 24.5$–150 eV. Description has been made on a high-temperature source of gaseous fullerenes and an efficient time-of-flight mass spectrometer. The absolute cross section curve is shown in Figure 1. The obtained cross sections were 762, 241 and 195 Mb at $h\nu = 24.5$, 90, and 110 eV, respectively with about 10% errors. The cross section curve was then normalized at $h\nu = 25$ eV to the absolute photoabsorption cross section reported by Jaensch and Kamke,\textsuperscript{1} the most reliable data so far available in the valence excitation region of C\textsubscript{60}. Accordingly, the present cross section data were altered to 407, 144 and 114 Mb at $h\nu = 25$, 90, and 110 eV, respectively.

Reference

**Figure 1.** Ion yield curves of C\textsubscript{60–2n+}+(n = 1–3) and C\textsubscript{60+} ions. Every tic mark indicates the appearance energy $AE(n)$ determined by, after subtracting an appropriate background, reading the photon energy at which the ion yield reaches 3% of the peak height of the curve.
VI-H-3  Photofragmentation of C$_{60}$ in the Extreme Ultraviolet: Statistical Analysis on the Appearance Energies of C$_{60-2n}^z$ ($n \geq 1$, $z = 1–3$)

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The ion yield curves for C$_{60-2n}^z$ ($n = 1–5$, $z = 1–3$) produced by photoionization of C$_{60}$ are measured in the photon energy ($h\nu$) range of 25–150 eV (see Figure 1). The appearance $h\nu$ values are higher by 30–33 eV than the thermochemical thresholds for dissociative ionization of C$_{60}$ leading to C$_{60-2n}^z$. Evaluation is made on the upper limits of the internal energies of the primary C$_{60}^z$ above which C$_{60-2n}^z$ + C$_2$ cannot escape from further dissociating into C$_{60-2n}^z$ + C$_2$. These upper limits agree well with the theoretical internal energies of C$_{60}^z$ corresponding to the threshold for the formation of C$_{60-2n}^z$ (see Figure 2). The photofragmentation of C$_{60}^z$ is considered to be governed by the mechanism of internal conversion of the electronically excited states of C$_{60}^z$, statistical redistribution of the excess energy among a number of vibrational modes, and sequential ejection of the C$_2$ units.

Figure 1. Ion yield curves of C$_{60-2n}^{2+}$ ions ($n = 1–5$) obtained from time-of-flight mass spectra.

VI-H-4  Fragmentation Mechanism of Highly Excited C$_{70}$ Cations in the Extreme Ultraviolet

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The ion yield curves for C$_{70-2n}^{z+}$ ($n = 1–8$, $z = 2$ and $3$) produced by photoionization of C$_{70}$ were measured in the photon energy ($h\nu$) range of 25–150 eV. The appearance $h\nu$ values were higher by ca. 34 eV than the thermochemical thresholds for dissociative ionization of C$_{70}$ leading to C$_{70-2n}^{z+}$. Evaluation was made on the upper limits of the internal energies of the primary C$_{70}^{z+}$ above which C$_{70-2n}^{z+}$ fragments cannot escape from further dissociating into C$_{70-2n}^{z+}$ + C$_2$. These critical internal energies agreed well with appearance internal energies of C$_{70}^{z+}$ theoretically obtained corresponding to the threshold for the formation of C$_{70-2n}^{z+}$ (see Figure 1). The photofragmentation of the parent C$_{70}^{z+}$ ions is considered to be governed by the mechanism of internal conversion of their electronically excited states, statistical redistribution of the excess energy among a number of vibrational modes, and sequential ejection of the C$_2$ units.

Figure 1. Fractional abundance curves of C$_{70}^{z+}$ and C$_{70-2n}^{z+}$ ions at 25 $\mu$s after photoionization of C$_{70}$ obtained by using the RRKM model to calculate the rate constants for reaction C$_{70-2n}^{z+}$ ($n \geq 1$) $\rightarrow$ C$_{70-2n}^{z+}$ + C$_2$.

VI-H-5  4d $\rightarrow$ 4f Dipole Resonance of the Metal Atom Encapsulated in a Fullerene Cage: Ce@C$_{82}$

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The yield curves for photoions from Ce@C\(_{82}\) are measured by using synchrotron radiation in the photon energy range from 90 to 160 eV. Parent Ce@C\(_{82}\)\(^{z+}\) and fragment ions C\(_{60}\)\(^{z+}\) and C\(_{70}\)\(^{z+}\) are observed in a mass spectrum (\(z = 1\) and 2) as shown in Figure 1. The yield curves for doubly-charged ionic species exhibit broad resonance in the photon energy region of from 120 to 140 eV which is ascribed to the \(4d \rightarrow 4f\) giant dipole resonance of the encapsulated Ce atom. The total photoabsorption cross section of Ce@C\(_{82}\) was determined from partial photoionization cross sections for formation of the parent and fragment ions to be 5.3±1.8–1.1 and 19.6±6.5–3.9 Mb at photon energies of 110 and 130 eV, respectively.

Figure 1. Time-of-flight mass spectra of the Ce@C\(_{82}\)\(^{z+}\) (\(z = 1\) and 2) produced by photoionization of Ce@C\(_{82}\) at \(h\nu = 118, 124, \) and 142 eV. The average temperature of the sample holder was set to 392 °C. Most of C\(_{60}\)\(^{z+}\) ions arose from photoionization of C\(_{60}\) neutrals which were desorbed from the surface of mass spectrometer.

VI-H-6 Photoion Yield Curves of Dy@C\(_{82}\) in the Vacuum UV Region

The photon yield curves for Dy@C\(_{82}\)\(^{z+}\) (\(z = 1\) and 2) from Dy@C\(_{82}\) are measured by using synchrotron radiation in the photon energy range from 24.5 to 39.5 eV. Correction has been made to compensate the effect of transient change of the density of Dy@C\(_{82}\) in the interaction region, with the help of the yield curve of C\(_{60}\)\(^{z+}\) produced from C\(_{60}\) remaining as a trace impurity in the sample. The yield of Dy@C\(_{82}\)\(^{2+}\) in Figure 1 exhibits a gradually descending curve with a flat region at 30–33 eV, similarly to the yield curve of C\(_{60}\)\(^{+}\) from C\(_{60}\). The total photoabsorption cross section of Dy@C\(_{82}\) was evaluated to be \((1.2±0.4) \times 10^2\) Mb at the photon energy of 39.5 eV.

Figure 1. Yield curves of Dy@C\(_{82}\)\(^{z+}\) (solid square) and Dy@C\(_{82}\)\(^{2+}\) (open triangle) produced from Dy@C\(_{82}\) in the photon energy range from 24.5–39.5 eV. The spectra are taken at photon energy intervals of 0.5 eV. The solid and dashed curves represent the results of the least-squares fitting to the data points of Dy@C\(_{82}\)\(^{+}\) and Dy@C\(_{82}\)\(^{2+}\), respectively, using seventh order polynomial functions. The open circle symbols denote the yield curve of C\(_{60}\)\(^{+}\) from C\(_{60}\) measured by using the neat C\(_{60}\) sample.

VI-H-7 4d→4f Dipole Resonance of the Pr Atom in an Endohedral Metallofullerene, Pr@C\(_{82}\)

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Following our preceding paper on the photoion yield spectra of the endohedral metallofullerene, Ce@C\(_{82}\)\(^{1}\) photoion yield spectra of Pr@C\(_{82}\) were measured in the photon energy range 100–150 eV with the help of time-of-flight mass spectrometry. Parent ions, Pr@C\(_{82}\)\(^{+}\), Pr@C\(_{82}\)\(^{2+}\) and Pr@C\(_{82}\)\(^{3+}\) were observed in the mass spectra. Photoion yield spectra of Pr@C\(_{82}\)\(^{+}\) and Pr@C\(_{82}\)\(^{2+}\) were obtained from the mass spectra and are shown in Figure 1. The photoion yield spectra of Pr@C\(_{82}\)\(^{2+}\) showed a broad peak at 120–140 eV. The broad peak was assigned to the \(4d \rightarrow 4f\) giant dipole resonance of the encapsulated Pr atoms. Absolute photoabsorption cross sections of Pr@C\(_{82}\) were evaluated from the photoion yield spectra and found to be \(23.6±6.7\) at 110 eV (off-resonance) and \(35.0±6.3\) Mb at 130 eV (on-resonance).
The enhancement of photoabsorption due to the giant resonance was comparable to that in Ce@C₈₂. The shapes of the peaks in the Pr@C₈₂ spectra, which originated from interference effects induced by the fullerene cage, were, however, different from those in the Ce@C₈₂ spectra. This could be accounted for by that the interference effects depend on the interior metal atoms.

Reference

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**VI–I**  Kinetic Energy Analysis of the Fragment Ions Produced from Fullerenes

When fullerenes gain enough amount of energy through photoionization processes, primarily formed ions are known to undergo decomposition into fragment ions with even numbered carbon atoms via sequential loss of C₂ units. We have measured the yield curves for C₆₀–2n⁺ from C₆₀ as a function of the internal energy of the parent C₆₀⁺ ions to study the mechanisms and kinetics of the sequential unimolecular reactions. These experimental yield curves have been compared with the theoretical fractional abundance curves which have been derived by employing the RRKM theory to every process of the sequential reactions: C₆₀–2n⁺ (n ≥ 1) → C₆₀–2n⁺ + C₂. To a first approximation the critical activation energies of the reactants C₆₀–2n⁺ were assumed to be equal to their binding energies for the above reactions. Indeed the experimental and theoretical curves provide almost the same appearance energies for the formation of C₆₀–2n⁺ (n ≥ 1). More reliable calculations of the rate constants of the individual reactions are needed before closer comparison between the two curves will be made. For such calculations we must know precise values of the activation energies for the reactions, together with the vibrational spectra of the transition states. This induced us to develop a new ion spectrometer for the fragment ions produced from C₆₀⁺ and C₇₀⁺. We wish that the magnitude of the potential barriers of the reactions can be estimated from the average kinetic energy release measured by this spectrometer.

VI–I–1  Development of the Photofragment Imaging Apparatus to Measure Scattering Distributions of the C₆₀–2n⁺ and C₇₀–2n⁺ Fragments Produced by Dissociative Photoionization of C₆₀ and C₇₀

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In dissociative photoionization of solitary fullerenes (C₆₀, C₇₀), we have measured the photofragment (C₆₀–2n⁺, C₇₀–2n⁺) yield curves in the photon energy range of 45–150 eV.¹ From the results we concluded that the excess energy is statistically distributed among the internal degrees of freedom of the parent ions (C₆₀⁺, C₇₀⁺) and C₂ units are ejected sequentially. Moreover, the results imply that the dissociation has no barrier and that no resonant state participates in the dissociation. To clarify these implications, we designed the photofragment imaging apparatus on the basis of the time-of-flight mass spectrometer that we had constructed. From the photofragment images, we can extract the kinetic energy and angular distributions of the photofragments. These distributions reveal clearly whether there exist a barrier and/or resonance.
We adopted the Eppink-Parker type velocity focusing electrodes\(^2\) to achieve the energy resolution on the images to resolve less than 0.1 eV increase by the photofragmentation. To select a bunch of fragments having a desired mass from neighboring bunches, for example, selecting $C_{66}^+$ from the consecutive masses such as $C_{68}^+$, $C_{66}^+$ and $C_{64}^+$, we designed a “mass gate” which consists of a potential switch and retarding electrodes. In order to optimize the dimensions of the setup, we performed ion trajectory simulations utilizing SIMION 7.0 software. The most suitable dimensions were obtained already and are schematically illustrated in Figure 1.

The operation principle of this setup is as follows. As long as the tube of the potential switch is kept grounded, all fragments are reflected back by the retarding electrode and do not hit an imaging detector. When an entire bunch of fragments having a desired mass enters inside the tube, the pulsed voltage is applied to the tube. The potential felt by the bunch are suddenly elevated and the bunch passes through the retarding electrode and thus hits the imaging detector.

Parts of this setup are being fabricated at the machine shop in IMS. The parts will be installed in the end-station at the beam line 2B in UVSOR. We are planning to examine the performance of the setup using SF$_6$ as a standard sample.

References

Figure 1. Schematic illustration of the photofragment imaging apparatus. A, repeller and extractor; B, potential switch; C, retarding electrodes; D, imaging detector.