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Photoion yield curves of $Dy@C_{82}$ in the vacuum UV region

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Abstract

The photoion 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 $Dy@C_{82}^{+}$ 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 $(1.2 \pm 0.4) \times 10^{-20}$ m^2 at the photon energy of 39.5 eV.

Keywords: Metallofullerenes; Metal endohedral fullerenes; $Dy@C_{82}$; Photoabsorption; Vacuum ultraviolet

1. Introduction

Because of an interest in the optical response of solitary fullerenes several investigations have been performed on the photoion yield curves of C_{60} and C_{70} in the gas phase [1–5]. Hertel et al. have observed remarkable peaks lying at $h\nu \sim 20$ eV in the yield curves of C_{60}^{+} and C_{70}^{+} from C_{60} and C_{70}, respectively, and attributed the peaks to a giant plasmon resonance [2]. Kou et al. have measured the yields of C_{60}^{+} from C_{60} covering a range of $h\nu$ as wide as 23–180 eV [3]. Below 50 eV they found several peaks and shoulders in the high-energy side of the 20 eV resonance. Similar experimental observation has been reported for C_{70} [4]. The spectral features in the curve of C_{60}^{+} reflect the molecular character of C_{60} and agree well with those in the calculated photoabsorption cross section of C_{60} reported by Colavita et al [6] who have clarified many fine structures at $h\nu = 16$–50 eV arising from single-electron excitations enhanced by shape resonances.

The interesting variation of the fullerene is the compounds made up of a cage of carbon atoms encapsulating one or several metal atoms inside the cage [7], so-called metal endohedral fullerenes $M_m@C_n$ ($m = 1, 2, \ldots$; $n = 60, 70, 80, 82, 84, \ldots$). Among various metal endohedral fullerenes, active studies have been devoted to elucidate geometrical structures and electronic properties of metal endohedral C_{82} [8–11], because a purified sample is acquired more readily for $M@C_{82}$ than for other type of metal endohedral fullerenes. Hence, expectations from manifold research fields rise high that $M@C_{82}$ provides possibilities of applications toward materials of novel functionalities such as nanoscale electronic devices [9]. Nevertheless, due to the difficulties in large-scale production of the pure sample, there had been no experimental work on the optical properties of gas-phase $M@C_{82}$ fullerenes in the vacuum UV and soft X-ray regions, until our report of the 4d → 4f dipole resonance of $Ce@C_{82}$ was published in 2005 [12].

The present paper describes the photion yield curve of $Dy@C_{82}^{+}$ and $Dy@C_{82}^{2+}$ produced from $Dy@C_{82}$ in the photon energy range of 24.5–39.5 eV. Within an assumption that the quantum yield, η, for photoionization is equal to

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unity,[1] the sum of the yields of these ions is considered to be nearly proportional to the total photoabsorption cross section of Dy@C_{82}. A few theoretical studies have been carried out dealing with the photoabsorption cross section of metal endohedral fullerenes. Wendin and Wästberg [13] have predicted several resonances at $h\nu = 15$–19 eV in the calculated photoabsorption spectrum of Ba@C_{60}. The spectrum shows a mixture of the nearly degenerate Ba 5p - 5d and C_{60} dipole resonances in which the Ba 5p shell and the C_{60} shells interact through out-of-phase and in-phase motions. In the case of Dy@C_{82} the $5p_{1/2}$ and $5p_{3/2}$ edges of the Dy atom are known to lie at 26.3 eV [14], so it is possible for us to tell whether or not the peak feature due to the Dy 5p - 5d resonance is modified by the fullerene cage.

2. Experimental and methods

A Dy@C_{82} sample was synthesized by the procedure reported by Kubozono and co-workers [11]. Soot containing Dy@C_{82} was prepared by an arc-discharge of a graphite composite rod with Dy concentration of 0.8 mol% under an ambience of 1.1×10^4 Pa buffer helium gas. The sample of Dy@C_{82} was extracted selectively with *N*,*N*-dimethylformamide (DMF) from the soot for 30 h by Soxhlet extraction. Black powder was obtained by removing DMF at 100 °C under reduced pressure (2.7×10^3 Pa). The powder was washed with *n*-hexane and the precipitate was dissolved into toluene by applying ultrasonic irradiation at 0–5 °C. The solution was filtered with a 0.2 μm membrane filter. After removing toluene, Dy@C_{82} was dried by dynamical pumping of 1×10^{-4} Pa at 200 °C for 3 days. Synthesis procedure of five working days resulted in about 5 mg of Dy@C_{82} with purity better than 90% from 10^{-2} kg of soot.

Identification of Dy@C_{82} was examined by using the laser-desorption mass spectrometry. Mass spectra contain a strong peak of Dy@$C_{82}{}^+$ with small amounts of Dy@$C_{80}{}^+$ and higher-order metal endohedral fullerenes Dy@$C_n{}^+$ ($n > 82$). A trace of $C_{60}{}^+$, $C_{70}{}^+$ and $C_{84}{}^+$ were also detected, the peak heights being the two orders of magnitude lower for these three ions than for Dy@$C_{82}{}^+$. At $m/z = 99$, 103, 129 and lower mass positions there exist prominent peaks of the fragment ions from the organic molecules secondarily produced during the Soxhlet extraction.

The experimental set-up for measurement of the photoion yields of Dy@C_{82} was described in detail elsewhere [4,12,15]. The sample powder was loaded in a quartz holder and a molecular beam was produced by heating the holder to approximately 460 °C. Monochromatized synchrotron radiation from a Dragon-type monochromator at the beam line 2B in UVSOR [16] was focused onto the molecular beam. The distance between the exit of the quartz holder and intersection region was 43 mm. The photon flux of the synchrotron radiation was estimated by measuring the photocurrent from a silicon photodiode. The sublimation rate of the sample was calculated from the deposition rate measured with a crystal-oscillator surface thickness monitor. A typical value of the sublimation rate was 0.2–0.4 ng s^{-1}. Thereby the number density in the interaction region was evaluated from the cross-section and average velocity of the Dy@C_{82} beam to be 1.2×10^{14} molecules m^{-3}.

The ionic species produced in the interaction region were extracted by a pulsed electric field (15 kHz, 100 V) with a duration of 5 μs, mass-separated by a double-focusing time-of-flight (TOF) mass spectrometer, and detected with a microchannel plate electron multiplier (MCP) connected to a conventional pulse counting system and a multichannel scaler. Ion signal counts were integrated over the respective mass peaks. The photoion yield curves were obtained by plotting the integrated counts divided by the photon flux as a function of the photon energy. On the contrary, no normalization has been made to the number density of Dy@C_{82}, because its very low sublimation rate led to large uncertainty due to the fluctuation in the reading of the thickness monitor. This issue will be discussed later. To inspect the dependence of the detection efficiency on the ion charge, we measured the ratios between the yield of Ar^+ (or Xe^+) and that of Ar^{2+} (or Xe^{2+}) at $h\nu = 70$, 80, and 90 eV. Next, we compared these values with the corresponding ratios reported by several workers [17,18] whose mass spectrometers were corrected for the transmission and detection efficiencies in advance. Since the intensity ratios in the present study are in good agreement with those in the literature within experimental uncertainties, no correction has been made for the detection efficiency.

3. Results and discussion

Fig. 1 shows time-of-flight (TOF) mass spectra for ions produced by photoirradiation of the Dy@C_{82} beam, measured at $h\nu = 39.5$, 33.5, and 25.0 eV for (a), (b), and (c), respectively. The peaks due to Dy@$C_{82}{}^{z+}$ and $C_{60}{}^{z+}$ ($z = 1$ and 2) are clearly observed. The resolution of the TOF spectrometer was not high enough for us to distinguish series of fragment ions, Dy@$C_{82-2n}{}^{z+}$ ($n \geq 1$) produced via the C_2-loss processes, from the parent Dy@$C_{82}{}^{z+}$ ions. However, the contribution of such fragment ions are considered to be negligible in the present photon energy region, because the excess internal energy deposited to the parent ions is redistributed effectively among a number of vibrational modes. By analogy with photoionization of C_{60} [19] one can expect that the excess energies more than 40 eV are required for the formation of Dy@$C_{82-2n}{}^{z+}$.

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[1] Considerable data on η have been accumulated for various molecules because of the interest in competition between direct ionization and excitation to their superexcited states opening to autoionization and neutral dissociation [22]. These data suggest that η-values increase with increasing photon energy and reach unity at the energy range above ∼23 eV. However, this statement is not necessarily acceptable for fullerenes, the electronically excited states of which may undergo rapid internal conversion leading to intramolecular vibrational redistribution and may escape from autoionization.

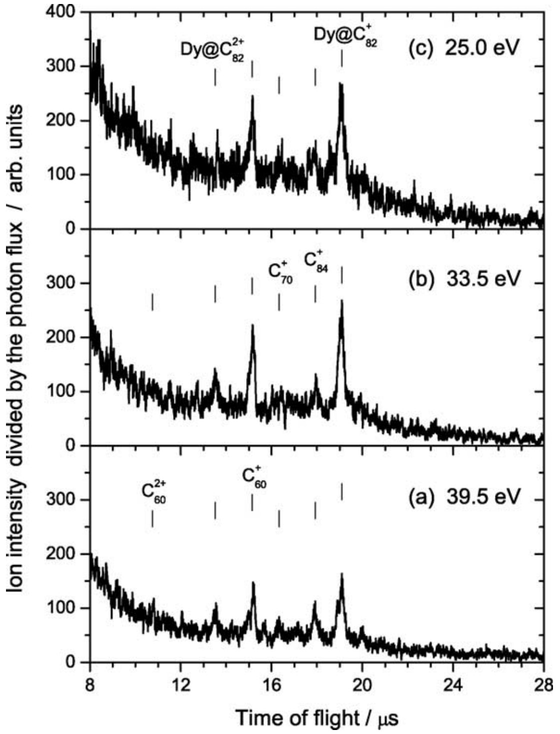

Fig. 1. Time-of-flight mass spectra of the Dy@C$_{82}{}^{z+}$ ($z = 1$ and 2) produced by photoionization of Dy@C$_{82}$ at $h\nu$: (a) 39.5 eV, (b) 33.5 eV, and (c) 25 eV. The average temperature of the sample holder was set to 460 °C. Fullerene ions, C$_{60}{}^{z+}$, C$_{70}{}^{+}$ and C$_{84}{}^{+}$ are considered to stem from C$_{60}$, C$_{70}$ and C$_{84}$, respectively, which remain in the Dy@C$_{82}$ sample.

The other two weak peaks at 16.3 and 17.9 μs are assignable to C$_{70}{}^{+}$ and C$_{84}{}^{+}$, respectively. Below TOF of ∼11.6 μs ($m/z \leq 420$) the mass spectra exhibit a rapid rise with decreasing m/z. This rise can be accounted for by the counts of the background ions with $m/z = 99$, 103, 129 that were formed after the rising edge of the pulsed electric field for ion extraction. In the TOF spectrum the signal of such photoions may spread over the pulse duration of 5 μs with respect to the proper positions of their mass peaks. On the other hand, it is not easy to understand the origins of a background ranging from 12 to 20 μs ($m/z = 450$–1250). We assume that this background results from single and double photoionization of other fullerenes and metal endohedral fullerenes such as C$_n$ ($n > 70$) and Dy@C$_n$ ($n \neq 82$).

Fullerene ions, C$_{60}{}^{z+}$ ($z = 1$ and 2), C$_{70}{}^{+}$ and C$_{84}{}^{+}$, in Fig. 1 are considered to stem from C$_{60}$, C$_{70}$ and C$_{84}$, respectively, which remain in the Dy@C$_{82}$ sample. Certainly, the preliminary examination by the laser-desorption mass spectrometry reveals contamination of trace quantities of C$_{60}$ and C$_{70}$ in the sample. Our previous investigation using neat C$_{60}$ has indicated the sublimation rate of 3–4 ng s^{-1} at ∼460 °C measured at the thickness monitor [15]. This rate is one order of magnitude higher than the typical sublimation rate of Dy@C$_{82}$ in the present study. Hence, it is fair to anticipate that the ion counts of C$_{60}{}^{+}$ and Dy@C$_{82}{}^{+}$ are roughly comparable, since the sublimation rate is remarkably higher for C$_{60}$ (and also for C$_{70}$) than for Dy@C$_{82}$.

In what follows we will describe the procedure to achieve the yield curves of Dy@C$_{82}{}^{+}$ and Dy@C$_{82}{}^{2+}$. A specific treatment has been given to compensate the influence of transient change of the density of Dy@C$_{82}$ in the interaction region. (1) The yield of Dy@C$_{82}{}^{+}$ or Dy@C$_{82}{}^{2+}$ at a certain photon energy was calculated from a TOF mass spectrum, by summing the ion counts over the mass peak, subtracting an appropriate background from the summed counts, and then dividing the net counts by the measured photon flux. Collecting the obtained ion yield consecutively with changing the photon energy at intervals of 0.5 eV allows us to depict a provisional yield curve. (2) The provisional yield curve of C$_{60}{}^{+}$ was determined from TOF mass spectra in a similar manner as above. (3) We compared this curve with a definite ion yield curve of C$_{60}{}^{+}$ [4], measured by using the neat C$_{60}$ sample with 99.98% pure, which is essentially equal to the relative partial photoionization cross section for production of C$_{60}{}^{+}$ from C$_{60}$. If the provisional yield of C$_{60}{}^{+}$ for the Dy@C$_{82}$ sample shows any deviation from the definite yield of C$_{60}{}^{+}$ at a certain $h\nu$, it is apparent that the number density of C$_{60}$, and therefore that of Dy@C$_{82}$, were subject to transient change probably on account of instability of the nozzle conditions when the monochromator reached this photon energy. (4) Correction factors were derived from the ratio of the C$_{60}{}^{+}$ yields between that for the neat C$_{60}$ sample and that for the Dy@C$_{82}$ sample including C$_{60}$. (5) We could achieve the yield curves of Dy@C$_{82}{}^{+}$ and Dy@C$_{82}{}^{2+}$ by multiplying the provisional yields by the correction factors.

Fig. 2 shows the yield curves of Dy@C$_{82}{}^{+}$ and Dy@C$_{82}{}^{2+}$ obtained through the above procedure. There are two sets of

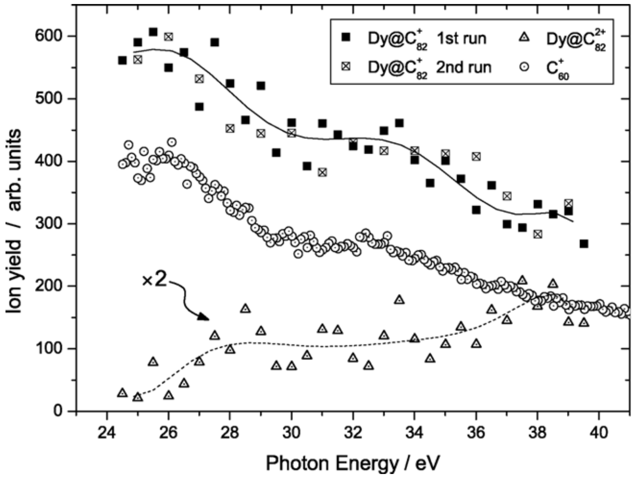

Fig. 2. Yield curves of the photoions produced from Dy@C$_{82}$ in the photon energy range of from 24.5–39.5 eV: (■) data points for Dy@C$_{82}{}^{+}$ from the first experimental run; (☒) those for Dy@C$_{82}{}^{+}$ from the second run; △, those for Dy@C$_{82}{}^{2+}$. The yield of Dy@C$_{82}{}^{2+}$ is made to double that of Dy@C$_{82}{}^{+}$. The spectra are taken at photon energy intervals of 0.5 eV. The yields are calculated from mass spectra in Fig. 1 and those at other photon energies. The solid and dashed curves represent the results of the least squares fitting to the data ☒ and △, respectively, using polynomial functions, and are to guide the reader's eye. The open circle symbols denote the yield curve of C$_{60}{}^{+}$ from C$_{60}$ measured by using the neat C$_{60}$ sample.

the yield data for Dy@C_{82}^+; (■) and (☒) taken in succession at almost the same temperature. These two sets of data accord fairly well with each other, which can demonstrate the validity of the above normalization method. The yield of Dy@C_{82}^+ forms a gradually descending curve with a flat region at 30–33 eV. The Dy@C_{82}^+ curve behaves similarly to the yield curve of C_{60}^+ measured by using the neat C_{60} sample, which is denoted by open circle symbols in Fig. 2. The flat region from 30 to 33 eV in the former curve may correspond to the shoulder at 31–34 eV in the latter curve. This suggests that both features have analogous origins. Our previous letter ascribed the shoulder 31–34 eV in the C_{60}^+ curve to transitions of an electron from an occupied valence orbital of C_{60} to a vacant orbital [3]. Hence, the flat region from 30 to 33 eV in the yield curve of Dy@C_{82}^+ is expected to arise from single electron excitation from molecular orbitals, which have large amplitudes near the carbon shell. No pronounced spectral anomaly has been found near the 5p edges of Dy at ∼26.3 eV. However, it is still too early to conclude that the Dy 5p - 5d resonance is smeared out by the giant resonance at ∼20 eV arising from heavy overlap of many shape resonances. This is because the Dy 5p - 5d resonance could shift to a lower energy below 24 eV outside of the photon energy region accessible by our monochromator.

The ion signal of Dy@C_{82}^{2+} is discernible above $h\nu \sim 27$ eV. Its yield curve almost levels off thereafter and shows a gradual rise at around 37 eV. Though nothing is known about the ionization potential of Dy@C_{82} for the formation of Dy@C_{82}^{2+}, this quantity can be conjectured from the threshold energies for double ionization of C_{60} and C_{70}, i.e. 19.0 and 18.84 eV, respectively [20]. If the ionization potential of Dy@C_{82} is close to those of C_{60} and C_{70}, the yield curve of Dy@C_{82}^{2+} probably behaves in a similar manner to those of C_{60}^{2+} and C_{70}^{2+}, at least in the onset region. Indeed, the shape of the Dy@C_{82}^{2+} curve in Fig. 2 is consistent with the increasing trend of the yields of C_{60}^{2+} and C_{70}^{2+} with increasing photon energy between 25 and 48 eV [4].

The photoionization cross sections of Dy@C_{82} for the formation of Dy@C_{82}^+ and Dy@C_{82}^{2+} ions were evaluated at $h\nu = 39.5$ eV from the count rate of the ion signal, photon flux of synchrotron radiation, number density of Dy@C_{82} in the ionization region, ionization volume, detection efficiency of our mass spectrometer, repetition rate of the pulsed electric field applied to the ionization region, and average residence time of the ions in the probed region where the pulsed voltage can guide them to the MCP detector [12]. The detection efficiency of the mass spectrometer was estimated from the total count rate of the ions C_{60}^{z+} ($z = 1$ and 2) produced from C_{60} at $h\nu = 39.5$ eV, by using the neat C_{60} sample, and the total photoabsorption cross section of sixty carbon atoms [21] there (1.94×10^{-20} m^2). The photoionization cross sections for formation of Dy@C_{82}^+ and Dy@C_{82}^{2+} from Dy@C_{82} thus obtained are $(9.7 \pm 0.3) \times 10^{-21}$ and $(2.5 \pm 0.1) \times 10^{-21}$ m^2, respectively. A large portion of the uncertainty arises from the fluctuation of the sample density owing to very low deposition rate of the thickness monitor. The sum of the above two cross sections, $(1.2 \pm 0.4) \times 10^{-20}$ m^2, is considered to correspond to the total photoabsorption cross section of Dy@C_{82} at $h\nu = 39.5$ eV.

The total photoabsorption cross section of Dy@C_{82} thus obtained is much smaller than that of 82 carbon atoms ($82\sigma(\mathrm{C}) = 2.66 \times 10^{-20}$ m^2 at $h\nu = 39.5$ eV) calculated from the carbon atomic cross section [21]. A striking discrepancy has also been found for the total photoabsorption cross section of Ce@C_{82} that we evaluated through a procedure similar to that described in the preceding paragraph [12]: 5.3×10^{-22} m^2 at $h\nu = 110$ eV against $82\sigma(\mathrm{C}) = 3.35 \times 10^{-21}$ m^2 at $h\nu = 108.5$ eV. We can give two explanations of why the cross sections of M@C_{82} (M = Dy and Ce) have been underestimated. First, it is possible that the detection efficiency for heavier M@C_{82}^+ is substantially lower than those for C_{60}^+ and C_{60}^{2+}. Conceivably our estimate of the total photoabsorption cross section of M@C_{82} needs to be revised upwards to some extent. Second, the number density of M@C_{82} at the ionization volume would be more diluted than expected from the deposition rate on the thickness monitor, probably because of poor collimation of the beam expanded from the nozzle and because of increase in the flow speed of the M@C_{82} vapor resulting from local-temperature rise at the nozzle throat. We are now planning to reduce the distance between the nozzle throat of the quartz holder and the photoionization region to increase the beam flux and obtain reliable evaluation of the number density of Dy@C_{82}.

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