Fluorescence of an organic-dye thin film by interaction with individual slow highly charged ions

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Fluorescence of an organic-dye thin film induced by the impact of individual slow iodine highly charged ions (HCIs) has been investigated for a wide range of charge states q from 30 (V-like ion) to 52 (H-like ion). Combined analysis of emission yields of the visible and x-ray photons reveal that L Auger electrons emitted in the neutralization process of the HCI play an important role in the electronic excitation of the target. It is also noted that, contrary to the energy dissipation of L Auger electrons, x rays carry away a large fraction of the potential energy of a HCI with higher q than the Ne-like ion.

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I. INTRODUCTION

Two categories of stopping power are well known for particles colliding on and into solids where the kinetic energy of the incident projectile is deposited along its trajectory in the solid. A fast (energetic) ion with sufficient "electronic stopping power" has the ability to excite the electronic system of the target. Here, the term "fast" means the velocity of the ion, v_{ion}, is much larger than the Bohr velocity, v_{Bohr}. For a slow ion ($v_{\mathrm{ion}}<v_{\mathrm{Bohr}}$), on the other hand, "nuclear stopping" dominates the dissipation process of the kinetic energy. This means the energy is dissipated not in electronic excitation but in the displacement of the target atoms one after another by the so-called knock-on collision.

Nevertheless, the possibility of electronic excitation has been noted in a collision of a slow highly charged ion (HCI) with a target even when the velocity is less than v_{Bohr} [1–3]. This is because the HCI interacts strongly with the electrons of the target, and ample potential energy E_{P} stored in the HCI is dissipated. Here E_{P} is defined as the total energy for producing the ion, which increases rapidly with charge state q of the HCI. For example, E_{P} for a hydrogenlike I^{52+} ion employed in this work reaches 150 keV. The strong coupling of the HCIs with the electronic system induces various effects such as emission of secondary particles (electron, ion, and neutral atom) and surface modification, which become highly prominent with increasing q. Although uv and/or visible photons from a sputtered neutral atom and x rays from a deexciting HCI have been observed [4,5], fluorescence from a bulk target due to the interband transition has never been observed thus far despite the close relation of such secondary effects to the strong electronic interaction.

This paper reports on the first observation of fluorescence from a target excited by individual slow I^{q+}-HCI impacts ($v_{\mathrm{HCI}}\sim 0.3v_{\mathrm{Bohr}}$). An organic thin film made of bis-MSB [1,4-bis(2-methylstyryl)benzene] dye molecules are chosen as a target. The present experiment has a clear advantage with the combination of the organic-dye thin film with high fluorescence yield and the HCIs up to very high charge state ($q=52$). By comparing q dependences of the fluorescence yield and x-ray photon yield, it is found that a specific deexcitation channel of the HCI, i.e., L Auger electron emission, plays an important role in the electronic excitation of the target. Other channels of the E_{P} dissipation are also investigated, showing that x rays carry away a large fraction of the E_{P} to the vacuum; the fraction is much larger than that estimated until quite recently [6,7].

II. EXPERIMENT

The bis-MSB was deposited onto an ITO (indium-tin-oxide) substrate in a preparation chamber. The deposition was performed at a rate of 5 Å/s and was stopped when the thickness of the film reached 50 nm. After the deposition, the sample was removed from the chamber and immediately installed in a collision chamber. I^{q+}-HCIs were produced in an electron beam ion trap (EBIT) at the University of Electro-Communications [8]. Figure 1(a) shows an experimental setup for obtaining a luminescence spectrum. The bis-MSB thin film was excited with irradiation of the high intensity HCI beam for which charge states were not separated; the charge states were mostly Ne- to He-like ions obtained by the EBIT operation with an electron beam energy of 48 keV [9]. From the back side of the substrate, light waves emitted from the bis-MSB were incident on the input port of an optical fiber and introduced to a 32-cm spectrometer equipped with a charge-coupled device (CCD) detector cooled to −120 °C. To measure the q dependence of the emission yield for visible photons Y_{V} from bis-MSB, a photon counting experiment was carried out using a photomultiplier tube (PMT, R1878, Hamamatsu Photonics K.K., Japan) as shown in Fig. 1(b). HCIs with a desired charge state were selected by a sector magnet and transported to the collision chamber. Many secondary electrons are emitted in a single HCI-impact event. The electrons were efficiently detected by an annular-type microchannel plate (MCP) fixed on the incident beam axis, while a bias voltage of −500 V was

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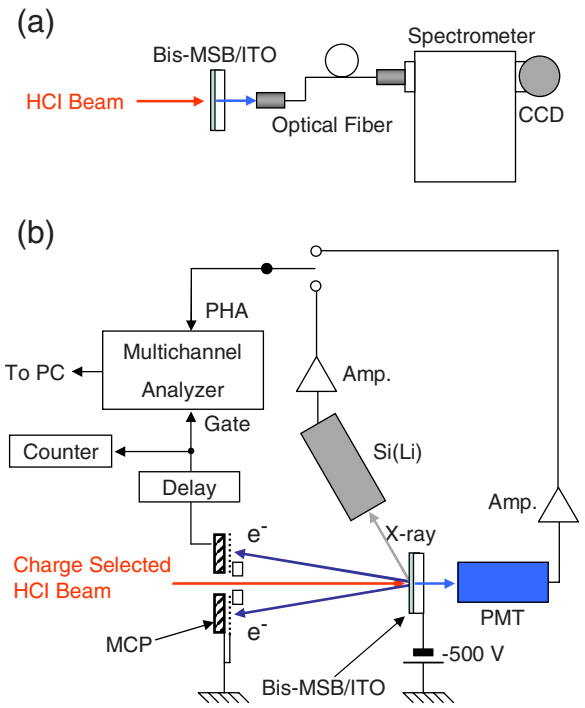

FIG. 1. (Color online) Experimental setups for obtaining luminescence spectra (a) and for visible and x-ray emission yields (b).

applied to the ITO substrate. The signal of the MCP from a bunch of electrons was used to count the number of incident HCIs and also used as a gate pulse to obtain the coincident signal from the PMT. The PMT was set on the back side of the substrate. Counting of single photon events was ensured by monitoring the pulse height distribution (PHD) of the signal from the PMT, using a multichannel analyzer. The distance between the sample and the photocathode of the PMT was properly adjusted so that more than one photon cannot hit the photocathode simultaneously in the event of individual HCI impacts. Indeed, higher pulse height components appeared in the PHDs with decreasing distance. This means more than one photon was simultaneously emitted by individual HCI impacts.

The emission yield Y_V was evaluated using the following relation:

$$\frac{N_w - N_{wo}}{N_{HCI}} = Y_V \frac{\Omega}{4\pi} C_{eff}, \tag{1}$$

where N_{HCI} is the number of incident HCIs and N_w and N_{wo} are photon counts from HCI-bombarded targets with and without the bis-MSB thin film, respectively. Ω is the solid angle of the observation estimated from the effective area of the photocathode (13 mm^2) and the distance between the sample and photocathode (18 mm). C_{eff} is the detection efficiency including the quantum efficiency of the PMT (10%) and transmission of the ITO substrate (80%).

III. RESULT AND DISCUSSION

Figure 2 shows a luminescence spectrum from the bis-MSB thin film excited by the HCI beam. This spectral shape

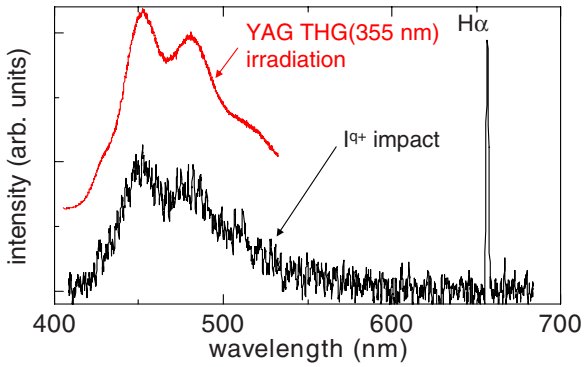

FIG. 2. (Color online) Black line: Luminescence spectrum from the bis-MSB thin film excited with HCI beam. Red (dark gray) line: Photoluminescence spectrum obtained with THG from YAG laser excitation.

is very similar to a photoluminescence spectrum obtained with the 355 nm third harmonic radiation (THG) from a Q-switched Nd:YAG laser shown as the red (dark gray) line. Clearly different from the photoluminescence the HCI-impact fluorescence has a sharp peak at 656 nm. This line was assigned as the Balmer α line (H_α) of the hydrogen atom sputtered from the bis-MSB thin film. The contribution of this peak intensity to the emission-band structure is less than 1% and no other atomic lines due to emission from sputtered particles or incident ions were observed. This implies almost all photons in the visible region originate from the interband transition of the bis-MSB thin film excited by the HCI impacts.

Figure 3 shows the visible photon emission yield Y_V measured for two sets of kinetic energies: E_K of $3.5q$ keV (solid circles) and $5.0q$ keV (triangles). Results were obtained for a wide q range from $q=30$ (V-like iodine ion) to 52 (H-like ion) and the circles indicated by black and red (dark gray)

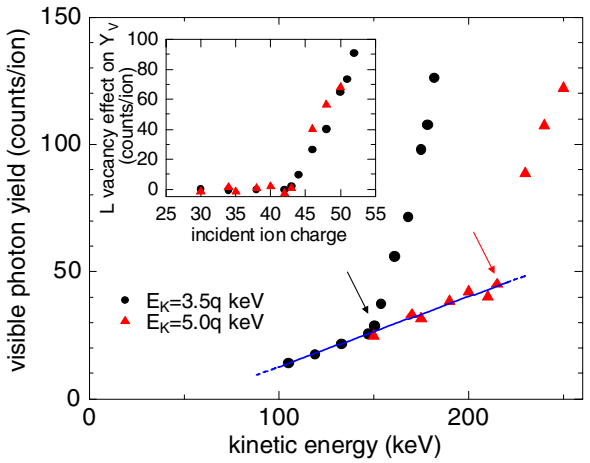

FIG. 3. (Color online) Relation of visible photon emission yield Y_V to the kinetic energy of I^{q+}, obtained with two sets of results: $3.5q$ (black circles) and $5q$ keV (triangles). Arrows represent data obtained with Ne-like I^{43+} impacts. The inset shows the L vacancy effect on Y_V obtained by subtracting the contribution of the kinetic effect estimated from the blue (dark gray) line as a function of incident charge state q.

arrows correspond to the results obtained with Ne-like I^{43+} impacts. In both yield curves, a sharp bend is found around $q=43$; Y_V increases linearly with q, that is with E_K, up to $q=43$ and then rises steeply with increasing q.

The gentle increase of Y_V for $q<43$ is considered to originate partly from the nonzero electronic stopping power of the incident projectiles. It is well known from the Lindhard-Scharff formula that an electronic stopping power S_e is proportional to v_{ion}, that is, $\sqrt{E_K}$, for the slow ion. The quasilinear increase of Y_V shows that the slope is larger than that expected from kinetic effect, which suggests that the electronic excitation results not only in kinetic energy dissipation but also in potential energy dissipation.

According to the classical over-the-barrier model [10], in the interaction of a slow HCI with a surface, the electron transfer begins above the surface. The target electrons are captured at high Rydberg states of the HCI, which subsequently becomes the so-called "hollow atom." Almost all the secondary electrons are emitted from the deexciting hollow atom. Low-energy electrons are emitted through cascading Auger transitions between the high Rydberg states. When the hollow atom arrives at the surface, further low-energy electrons are emitted from the Rydberg states by the "peel off" process [11]. Thus, many secondary electrons are emitted in the HCI interaction, having mostly low energies ($<\sim 20$ eV). These electrons would contribute to excite the electronic system of the bis-MSB thin film which emits visible photons. Consequently, the Y_V shows a more steep increase with q compared to the kinetic effect with $v_{ion}(q)$ because the number of secondary electrons increases sharply with q.

For $q>43$, it can be seen that, in addition to the minor contribution of the kinetic energy of an incident HCI and low-energy secondary electrons as mentioned above, the potential energy of HCIs with L shell vacancies has a distinguishable effect. Ne-like I^{43+} has the closed-shell structure of $1s^22s^22p^6$ whereas vacancies in the L shell are present for I^{q+} with $q\geqq 44$. To emphasize the L shell vacancy effect, the inset in Fig. 3 shows the fluorescence yield obtained by subtracting the contribution of the kinetic effect estimated from the blue (dark gray) line in Fig. 3. It is surprising that the secondary photon emission from the target is clearly correlated with the electronic shell structure of the incident HCIs. It has never been observed in investigations on secondary emission yields for other secondary particles such as electrons [11] and ions [12,13]. For example, in our previous study on proton sputtering from a hydrogen-terminated Si surface bombarded with I^{q+}-HCIs [13], it was found that while the sputtering yield of H^+ depends strongly on q, it increases smoothly with q in the wide q region from 17 to 53 (fully stripped ion), that is, no sudden change is shown around $q=43$ (Ne-like) and $q=51$ (He-like). The secondary electron emission yield measured by Kurz *et al.* [11] similarly shows a gradual increase with q in the wide q region. These results suggest that visible photon emission resulting from electronic excitation of the target arises from a qualitatively different mechanism to those that have been observed so far.

The individual L shell vacancies are filled by the intra-atomic transition of either radiative or Auger transitions in the neutralization process of the HCI. The transition to L shell vacancies, which might occur mostly below the surface along the HCI trajectory, contributes to the potential energy deposition for I^{q+} with $q\geqq 44$ through L x-ray and Auger electron emissions and more or less induces the electronic excitation of the target. To discuss the contribution of the intra-atomic transitions in HCIs to the fluorescence yield, the ratio of the L x-ray to the L Auger transitions was investigated by measuring the x-ray emission from the deexciting HCIs. The detailed method of the x-ray observation has been reported elsewhere [5]. Figure 4(a) shows typical x-ray spectra obtained with I^{q+} impacts. Black, red, green, and blue lines correspond to the spectra from $q=52$ (H-like), 49 (Be-like), 46 (N-like), and 44 (F-like) ions, respectively. The spectra are important to know the energy ranges of x rays propagating in the target although they are very similar to that already reported in Ref. [5]. For H-like ion, the Rydberg series of K x rays can be seen in the energy region from 28 to 40 keV in addition to the L x-ray series below 10 keV. The peaks of the L x-ray series cannot be observed well separated due to the low resolution of the detector. Note that the energy region below 3.7 keV for M x rays is truncated because it could not be properly measured due to the strong attenuation by the Be window of the detector.

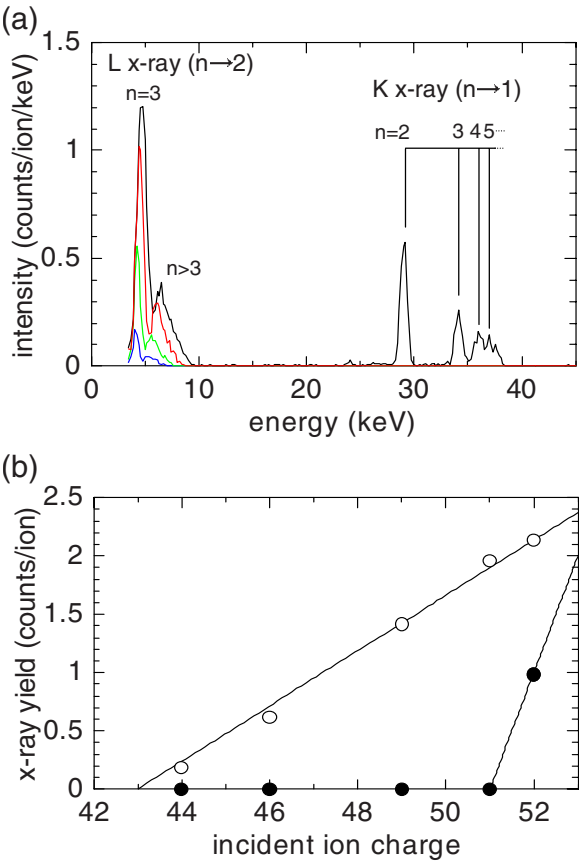

FIG. 4. (Color online) (a) X-ray spectra obtained from I^{q+} colliding with the bis-MSB film ($q=44$, 46, 49, and 52). (b) Emission yields for K (solid circles) and L (open circles) x rays as a function of q. Lines are drawn as visual guides.

The x-ray emission yields of K x rays (Y_{Kx}) and L x rays (Y_{Lx}) are evaluated by numerically integrating over the cor-

responding energy regions of spectra. Y_{Kx} and Y_{Lx} are plotted as functions of q in Fig. 4(b). It is found that since $Y_{Kx}=1$ for the H-like I^{52+} ion, the K shell vacancy is filled completely through radiative transition, or in other words, no K Auger process occurs. To the contrary, the L Auger process becomes the dominant atomic transition in filling L shell vacancies. For example, as is clear from the result of $Y_{Lx}\sim 2$ for the He-like I^{51+} ion, eight vacancies in the L shell are filled by two radiative transitions and six L Auger transitions. The fraction of these filling processes for K and L shell vacancies is governed by their competitive transition rates [14].

The intra-atomic processes of radiative and/or Auger transitions would be responsible for the dramatic change in the q dependence around $q=43$ shown in Fig. 3. To find the contribution of L x ray (3–10 keV) to the fluorescence yield Y_V, the fluorescence yield Y_{VFe} of the thin film excited by x rays (5.9 keV) from a ^{55}Fe radioisotope source was measured. Y_{VFe} was evaluated to be ~ 5 from the relation $\frac{N_w-N_{wo}}{N_{x\ ray}}=Y_{VFe}\frac{\Omega}{4\pi}C_{eff}$, using our experimental parameters and the intensity of the source $N_{x\ ray}$. This result implies that the L x ray is a minor contributor to the excitation of the target. For example, because $Y_{Lx}\sim 2$ for the He-like I^{51+} ion, a small fraction of only 10 out of 110 of Y_V comes from L x-ray emission. This is a reasonable result in that the bis-MSB has a small attenuation coefficient ($\sim 10\ cm^{-1}$) for the L x-ray energy region. It is therefore concluded that the dominant process for excitation of the electronic system of the target is not the radiative transition but Auger transition.

L Auger electrons emitted only for the incident HCIs with $q\geqq 44$ have sufficient energies to excite the target electronic states even though their numbers are smaller than those of the low-energy secondary electrons. For the L shell filling process, Auger transitions ($\sim 75\%$) dominate the radiative transitions ($\sim 25\%$) as can be seen from Fig. 4(b), where the number of active L Auger electrons that can excite the target increases with q. Consequently, as seen in Fig. 3, Y_V has a rapid increase from $q=44$. As a result, the fluorescence yield shows a quasilinear increase proportional to q ($\geqq 44$). The potential energy (E_P) dissipates through the L Auger electron emissions that induce other kinds of elementary excitations, e.g., phonon, in addition to the present target electronic excitation.

It is useful for understanding a feature of the HCI-surface interaction to discuss the density of electronic excitation by the HCI impact. Although it is hard to separate completely the effects of two kinds of energy relaxation processes; kinetic and potential energy (E_K and E_P) dissipations, it is seen that these processes are different in the interaction volume (V_i). For E_K dissipation, V_i that increases with E_K distributes along the trajectory of the ion in the target. Here, the electronic stopping power is an important parameter for the density of the electronic excitation, which is proportional to $\sqrt{E_K}$. For E_P dissipation, on the other hand, V_i is restrict to the surface layers even E_P (or q) increases. Low-energy electrons emitted from a hollow atom near the surface have the very short mean-free-path (typically a few Å) [15]. Further, the number of the low-energy electron increases with q, keeping the relative energy distribution similar. Therefore, the density of the electronic excitation should increase with q. For $q>43$, in addition to the low-energy electron effect, the energy dissipation channel by L Auger electrons is opened as the L shell vacancies are created. The mean free path of the electron gently increases with the electron energy and reaches typically 10 Å for the high-energy LMM Auger electron having ~ 3 keV from I^{q+}. It is found, even though the higher-energy electron has the longer mean free path, the energy loss per length for the high-energy electron, which reaches a few hundreds eV/Å, should be larger than that for the low-energy electron (~ 10 eV/Å). Therefore, the number of excited molecules would be dramatically enhanced in the impact of HCIs with higher q than Ne-like ion ($q=43$).

It should be noted that the lifetime of a excited dye molecule, which is typically subnanoseconds or longer, is much longer than the relaxation time of a HCI interacting with a surface (much less than 100 fs, e.g., about 7 fs for Xe^{44+} and Au^{68+} on carbon foils [16]). Therefore, many excited molecules would still exist in the interaction region after the energy dissipation of the HCI. This situation is similar to that induced by intense, ultrafast laser irradiation, although excitation processes are quite different. Effects of the high density excitation on the response of the target involve interesting physical phenomena such as structural instability, exciton condensation, and so on. Further investigations including the time-resolved measurement for the post-interaction phenomena should be important to understand differences between HCI excitation and laser excitation.

Finally, the E_P dissipations in the interaction of I^{q+} ions ranging from $q=43$ to 51 that have 0 to 8 L $(2s,2p)$ vacancies and of I^{52+} with one K $(1s)$ vacancy are discussed. While the dissipated fractions of E_P from x-ray emissions were found to be from 0 to 10% (0–11 keV) from $q=43$ to 51 [5], those from L Auger electrons having energies of a few to several keV are estimated to increase to more than 30% (about 40 keV) toward $q=51$, which might be the dominant E_P-dissipation channel in this q region. On the other hand, there is a large difference in the potential energy between He-like I^{51+} (110 keV) and H-like I^{52+} (150 keV) ions, which originates from the tight binding energy of the $1s$ electron (~ 40 keV). Nonetheless, no discrete increase in the q dependence of Y_V is observed from $q=51$ to 52 as shown in Fig. 3. This result implies that most of the large potential energy from the ionization of the $1s$ electron is dissipated through the emission of a high energy K x-ray photon (~ 32 keV) with $Y_{Kx}=1$. The K x ray would not contribute to the excitation of the electronic system of the bis-MSB thin film composed of only carbon and hydrogen atoms because such a high-energy photon is hardly absorbed by these light atoms and hence the K x ray is transparent for the target materials. It is, therefore, concluded that even when the high-energy K x ray is emitted in a H-like I^{52+} impact, the Y_V curve shows a gradual and continuous increase from $q=43$ to 52 without any steep rise. It has been believed until quite recently [6,7] that the fraction of outgoing energy carried away by sputtered ions and neutral atoms, electrons, x rays, and so on was less than 10% of E_P. It is, however, seen in the present study for very high q HCI interactions that x rays carry away a large fraction of E_P to vacuum with no interaction with the target. The fraction of E_P dissipated through x-ray emission reaches 10% for He-like I^{51+} and 30% for H-like I^{52+}.

IV. CONCLUSION

Visible light emissions were observed from a bis-MSB target that was excited electronically in the interaction with a "slow" HCI of iodine. The q dependence of the fluorescence yield is remarkable in that it exhibits the sharp increase started at $q=43$, clearly correlated with the electronic shell structure of the incident HCI. It is concluded that L Auger electrons emitted in the neutralization of the HCI along its trajectory play an important role in the target excitation. Since the L Auger transitions give a large contribution to the dissipation of the potential energy (E_P) of the iodine-HCIs for F-like to He-like iodine ions, the observation of visible light emission would be a good indicator of the E_P dissipation of the target.

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